A Relationship between the Associating Power of Optical Isomers, and the Formation of Racemic Compounds.

T H E S I S

submitted for the degree of D.Sc.,

by

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I N D E X.

I N T R O D U C T O R Y.

The question as to the existence of racemic compounds, when two optical isomers are mixed in equal quantity, has proved to be one of considerable difficulty. The mere crystallographic examination was shown to be inadequate, and in the course of their investigation Kipping and Pope showed that it was possible to have another type of crystal, besides the pure racemate, and the crystals of the d- & l- isomers, namely a pseudoracemic crystal. Later it was also demonstrated that the determination of the melting points of the pure isomers and of the 50% mixture of them was not sufficient to settle the question.

It was not till Roozeboom [Zeit. Phys. Chem. 1899, 28, 494] took up the question from the point of view of the Phase Rule that the subject was put on a satisfactory footing. In his classical contribution he investigated the subject both from the point of view of solubility curves and of melting point curves. We only propose to consider the latter type of curve at present. He showed that /

that there were three main types of curve to be expected, (a) the mixed crystal curve, which would be a continuous curve joining the melting points of the two isomers, and in its simplest form would be a straight line; (b) a curve consisting of two parts giving a minimum of temperature at their point of intersection; and (c) a curve giving two minima (eutectic points) and a maximum point. The type (a) represents the pseudoracemic mixed crystal, but does not preclude the existence of a racemic compound. Type (b) represents a simple mixture of d- and l- isomers, the so called d- and l- conglomerate. The type (c) represents the definite formation of a racemic compound. Later work such as that by Adriani [Zeit. Phys. Chem. 33, 453] has tended to confirm Roozeboom's conclusions. This work has shown that the presence of racemic compounds in the liquid state, at the temperature of melting, may be definitely proved by a complete study of the melting point curves of optical isomers.

While the general shape of the melting point curve of such isomers as have been studied has frequently been commented on, an exact mathematical /

mathematical analysis of the curves has not often been attempted. Kremann [Monat. 25, 1215] has shown how the degree of dissociation of the racemic compound may be calculated, and so a definite statement may be made as to the amount of racemic compound present in the liquid state. The calculations employed are not entirely free from objection, as is pointed out by Kremann himself, but at any rate they serve to give a very good indication of the correct result. The method has been applied by Findlay and Hickmans [J.C.S. 1907, 905] to the investigation of the melting point curve for menthyl mandelic ester.

Washburn and Read [Nat. Acad. Sc. 1915, 191] have suggested a formula which should yield the melting point curve for so called "ideal" solution. As mixtures of optical isomers fulfil the conditions of such "ideal" solutions, more exactly than any other, it was suggested that the melting point curves might be investigated from this point of view. A comparison of the results obtained by the Washburn and Read formula, by the Van't Hoff formula, and by the Raoult freezing point law will be discussed in the /

the course of this investigation. It should also be mentioned that Van Laar [Zeit. Phys. Chem. vols. 63, 64, 66] has worked out a mathematical treatment of the possible curves in great detail, starting from the fundamental relationships given by the Thermodynamic potential. From the evidence already accumulated it seemed unlikely that a definite answer could be given to the question as to whether a racemic compound should exist in the liquid state apart from considerations of the molecular nature of the optical isomers. If we find, for example, that a molecule of dextro isomer shows a tendency to unite with another molecule of dextro isomer to give an associated molecule represented by 2d, then it might be expected that a molecule of dextro isomer would unite with a molecule of laevo isomer to give a racemic compound, the racemic compound being analogous to the associated 2d molecule of the dextro isomer. If, on the other hand, the destro isomer shows little tendency to associate with itself, then we might expect that the racemic compound, if formed, would be largely dissociated into its components. To test these conclusions

a /

a number of related substances in the camphor series were investigated, viz.:-

d- & l- Borneol	Alcohol
d- & l- Camphor	Ketone
d- & l- Camphoric Acid	Acid
d- & l- Camphoric Anhydride	Anhydride
d- & l- Ortho Methyl Camphoric Ester	Acid Ester
d- & l- Bornyl Hydrogen Phthalate	Acid Ester
d- & l- Pinene	Hydrocarbon
d- & l- Camphene	Hydrocarbon

In general Hydrocarbons show no tendency to associate, and we should therefore expect no racemic compound in this case. The Anhydrides are generally in the same category, while the Ketones, Alcohols, Acid Esters, and Acids might be expected to show increasing tendency to form associated molecules, and so racemic compounds. It was hoped to apply to the melting point curves obtained for these substances a mathematical analysis, employing the various forms of equations for the curves, which have been suggested.

PREPARATION of OPTICAL ISOMERS.

Since the substances were to be used to determine melting points, special care was taken to obtain the dextro and laevo forms in as pure a state as possible. A Schmidt and Haensch instrument was used in all polarimetric measurements, which were carried out in a two decimetre tube at ordinary temperature using sodium light. c denotes the number of grams of substance dissolved in 100 c.c. of solution. All temperatures have been corrected for emergent stem, and comparisons made with a standard Thermometer.

B O R N E O L.

Laevo borneol.

This substance was obtained from the British Drug Houses Limited. After one recrystallisation from light petroleum ether, it melted at 207°C, and gave a rotation of $[\alpha]_D^{14.5} = -36.52^\circ$ in toluene solution with c = 11.5. A second sample gave $[\alpha]_D^{14.5} = -36.81^\circ$, while Haller gives $[\alpha]_D = -37.1^\circ$. This, however, was not sufficiently pure for our purpose, so a lengthy purification was carried out.

The /

The general method is due to Haller [C.R. 1889, 108, 456], and was also used by Pickard and Littlebury [J.C.S. 1907, 1974]. After suitable modifications that finally adopted was as follows:-

The l-borneol was first converted into l-bornyl hydrogen phthalate by heating it with phthalic anhydride to 130°C for two hours. Haller recommends a longer period of heating and the use of sealed tubes, but a better yield of the hydrogen phthalate was obtained by heating for two hours in a corked flask. The phthalate obtained was recrystallised from boiling benzene, and gave a rotation of $[\alpha]_D$ = -55.1° with c = 10 in absolute alcohol. The hydrogen phthalate was then coupled up with l-menthylamine hydrochloride, which was prepared from l-menthol. The l-menthylamine salt separated first as a pasty mass which soon hardened. After filtration it was dissolved in methyl alcohol. On dilution of this solution with a small quantity of water, the l-menthylamine l-bornyl phthalate crystallised out. Pure l-menthylamine salt was obtained by three further recrystallisations from methyl alcohol. It gave a rotation of $[\alpha]_D^{14.5}$ = -41.20° with c = 5 in methyl alcohol. Haller gives /

gives $[\alpha]_D = -52.80^\circ$. The hydrolysis of the pure l-menthylamine salt was effected by boiling with hydrochloric acid in alcoholic solution. The product was recrystallised from boiling benzene, melted at 163°C, and gave a rotation of $[\alpha]_D^{14.5}$ $= -56.1^\circ$ with c = 10 in absolute alcohol. Haller gives $[\alpha]_D = -58.27^\circ$. This purified l-bornyl hydrogen phthalate was used in the determination of the d and l-phthalate melting point curve. The hydrolysis of the pure l-bornyl hydrogen phthalate was carried out by boiling it on the water bath with a solution of potassium hydroxide dissolved in methyl alcohol. The l-borneol so obtained was recrystallised from light petroleum ether. It melted at 207.2°C and gave a rotation of $[\alpha]_D^{14.5} = -37.50^\circ$ with c = 8 in toluene. A similar purification carried out on a second sample of l-borneol, gave $[\alpha]_D^{19} = -37.65^\circ$. Haller gives $[\alpha]_D = -37.61^\circ$. The pure l-borneol so obtained was used in the determination of the melting point curve of d- and l-borneols, and also as a starting material in the preparation of l-camphor, l-camphoric acid, l-camphoric anhydride, and l-ortho methyl camphoric ester.

Dextro /

Dextro borneol was obtained from the British Drug Houses Limited. On recrystallisation from light petroleum ether, a product was obtained which melted at 206°C, and gave a rotation of $[\alpha]_D^{14.5} = +29.88°$ with c = 8 in toluene. For pure d-borneol Haller gives $[\alpha]_D = +37.77°$. The correct melting point and the appearance of the crystals seemed to indicate a pure product. The incorrectness of the rotation is accounted for by the fact that we were dealing with mixed crystals of d-borneol and l-isoborneol. This was shown by Mackenzie [J.C.S. 1907, 1225], but the fact that Lowry [J.C.S. 1925, 614] employs for polarimetric measurements d-borneol of low rotation indicates that this fact is not generally known. The d-borneol was boiled with zinc chloride in benzene solution to remove the isoborneol. The rotation of the product so obtained did not rise above 35°, so a purification similar to that employed in the case of l-borneol had to be carried out. The d-bornyl hydrogen phthalate was recrystallised from glacial acetic acid, and had a melting point of 161.4°C. The l-menthylamine d-salt was recrystallised four times from acetone before being obtained in a pure state. After hydrolysis /

hydrolysis the pure d-borneol obtained gave a rotation of $[\alpha]_D^{16} = +37.1^\circ$ with c = 8 in toluene, and had a melting point of 206.5°C.

C A M P H O R.

Laevo Camphor was obtained from the pure l-borneol prepared as above, by oxidising it with concentrated nitric acid. Aschan, [Acta Soc. Scientiarum Fennicae, Tom XX1 No. 5]. The l-camphor so obtained was recrystallised from benzene. It melted at 177.7°C, and gave a rotation of $[\alpha]_D^{16} = -43.61^\circ$, with c = 16.51 in absolute alcohol. Beckmann [L.A. No. 250, 253] gives $[\alpha]_D = -44.22^\circ$.

Dextro Camphor was obtained from the commercial product Camphor Ang.. On recrystallisation from alcohol it melted at 178.6°C, and gave a rotation of $[\alpha]_D^{16} = +44.20^\circ$, with c = 16.51 in absolute alcohol. Beckmann gives $[\alpha]_D = +44.22^\circ$. This sample was employed in all the experiments without further purification.

CAMPHORIC /

CAMPHORIC ACID.

Laevo Camphoric Acid was prepared from the pure l-borneol obtained as above, by oxidising it by heating ~~it~~ with concentrated nitric acid to 100°C on an electric heater for fifty hours. The crude acid was partly purified by converting it into the sodium salt, and reprecipitating the acid with concentrated hydrochloric acid. The product so obtained melted at 182.5° - 183°C, and gave a rotation of $[\alpha]_D^{16} = -45.41^\circ$ with c = 8.24 in absolute alcohol. Further purification was effected by converting the acid into camphoric anhydride, The anhydride was then treated with an aqueous solution of potassium carbonate, and the acid precipitated by addition of hydrochloric acid. The melting point was now 187.5°C, and the rotation was $[\alpha]_D^{16} = -48.12^\circ$ with c = 8.24 in absolute alcohol.

Dextro Camphoric Acid was obtained from the d-camphoric acid supplied by the British Drug Houses Limited. After one recrystallisation from aqueous alcohol it melted at 177°- 179°C, and gave a rotation of $[\alpha]_D^{16} = +47.15^\circ$ with c = 8.24 in absolute alcohol. It was further purified by converting into the anhydride /

anhydride, as in the case of the laevo acid. After this purification the melting point was 187.6°C, and the rotation was $[\alpha]_D^{17} = +47.6°$ with c = 8.24 in absolute alcohol. From camphoric anhydride obtained from the British Drug Houses Limited, d-acid of melting point 188.2°C, and rotation $[\alpha]_D^{17} = +47.75°$ with c = 8.24 in absolute alcohol, was obtained.

CAMPHORIC ANHYDRIDE.

Laevo Camphoric Anhydride was obtained in the course of the preparation of l-camphoric acid. After two recrystallisations from boiling alcohol, it melted at 222.9°C, and gave a rotation of $[\alpha]_D^{16} = +3.2°$ with c = 4 in benzene. It should be noted that the anhydride prepared from laevo camphoric acid is dextrorotatory, but the name "laevo" camphoric anhydride is retained to designate this substance.

Dextro Camphoric Anhydride was obtained in the purification of d-camphoric acid. After two recrystallisations from boiling alcohol it melted at 223.8°C, and gave a rotation of $[\alpha]_D = -3.1°$ with c = 4 in benzene. Mersh [Chem. News 60, 307] gives $[\alpha]_D = -3.7°$. In these experiments the name "dextro" camphoric anhydride is retained for this substance.

Ortho /

ORTHO METHYL CAMPHORIC ESTER.

Laevo Camphoric Ester.

This substance was prepared by two different methods. Firstly, by acting on l-camphoric anhydride with sodium methoxide Walker, [J.C.S. 1892, 1088]. The substance separated from aqueous solution as an oil, and even after drying no crystals appeared for several months. With later batches, however, the product crystallised readily on seeding with a crystal of l-ester. Once crystals had been obtained, and had been separated from the oil by pressing out on a porous plate, they could be recrystallised easily from light petroleum ether. The ester first prepared melted at 86°C, and showed no rotation with plane polarised light. It must have become racemised at some stage in the process. The laevo ester which was obtained later melted at 73.5°C, and gave a rotation of $[\alpha]_D^{15}$ = -52.95° with c = 10 in absolute alcohol. The ester was obtained in the second place by acting on l-camphoric acid dissolved in methyl alcohol with dry hydrochloric acid gas, which was passed in for about two hours. This ester first separated as an oil /

oil, but after recrystallisation from light petroleum ether after seeding with crystal of l-ester obtained as above, it gave a melting point of 73.5°C. Titration of the crystals in aqueous alcoholic solution with standard baryta gave 12.40 c.c. required (Theoretical = 12.58 c.c.).

Dextro Camphoric Ester.

This was prepared in a manner exactly similar to the l-ester. The oil which separated at first, after recrystallisation from light petroleum ether, melted at 63°C. By successive recrystallisations the melting point rose to 76°C. The ester gave a rotation of $[\alpha]_D^{15} = +51.95^\circ$ with c = 10 in absolute alcohol. Haller [C.R. 114, 1516]. gives a melting point of 75° to 76° C, and $[\alpha]_D = +51.52^\circ$. A titration with baryta solution showed that the oil had exactly the same composition as the pure crystals.

BORNYL HYDROGEN PHTHALATES.

The laevo and dextro forms of this were prepared in the course of purification of laevo and dextro borneols, and utilised after one recrystallisation from /

from their respective solvents, benzene and glacial acetic acid.

P I N E N E.

The optical rotation shown by this substance seems to depend on its source, see Landolt "Das Optische Drehungsvermogen", Second Edition pages 555-557. The method of purification adopted was that of repeated distillation in steam, a little carbonate being added to the pinene before starting, followed by drying and careful fractionation.

Laevo Pinene.

The sample used was obtained from the British Drug Houses Limited. The initial rotation was $[\alpha]_D^{15} = -35.23^\circ$, density = 0.8682. After purification the main fraction boiled at 160°C, and gave a rotation of $[\alpha]_D^{15} = -37.58^\circ$, density = 0.8674. It gave a sharp melting point at -63°C.

Dextro Pinene.

The dextro pinene used in these experiments was obtained from Kahlbaum. The initial rotation was $[\alpha]_D^{15} = +45.38^\circ$, density = 0.8665. After purification the main portion boiled at 156°C, and gave /

gave a rotation of $[\alpha]_D^{15} = +46.80^\circ$, density = 0.8590. It gave a sharp melting point at -64°C.

C A M P H E N E.

Laevo Camphene.

This substance was obtained from the pure l-pinene by converting it into pinene hydrochloride, and acting on the latter with potassium phenolate. After drying, the camphene was fractionated in a small fractionating column, using an air condenser. Pure l-camphene came over at 160.5°C, and melted at 44°C, while its rotation was $[\alpha]_D^{15} = -77.15^\circ$ with c = 10 in absolute alcohol. As in the case of the pinenes, the rotation seems to depend on the source of the product.

Dextro Camphene.

This substance was prepared from pure d-pinene in a manner exactly similar to the laevo camphene. It boiled at 160°C, melted at 46°C, and gave a rotation of $[\alpha]_D^{15} = +72.8^\circ$ with c = 11.7 in absolute alcohol.

DETERMINATION of CURVES.

Owing to the difficulty of obtaining the pure dextro and laevo isomers, used in those experiments, in large quantity, some method of obtaining the curves had to be devised which would permit of the use of small quantities of the substances. Moreover, since borneol for example does not melt till 206°C., yet boils as low as 212°C., and is consequently very volatile at its melting point, the investigation of the melting point curve had to be carried out in a closed tube. This made the arrangement for stirring a problem of some difficulty. As the temperatures ranged from -60°C. to 220°C., it was not easy to obtain accurate thermometers, which would cover all the range. The use of a thermocouple was therefore decided upon, since it would be equally accurate throughout the whole range.

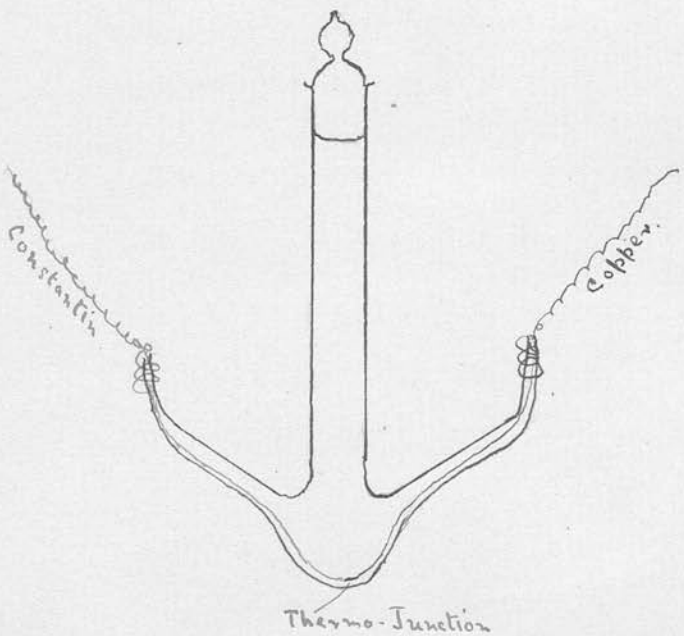
THE TUBE.

The determinations were carried out in a specially prepared tube. A bulb was blown on the end of a glass tube six inches long and half an inch in /

in diameter. Two side tubes three inches long and one eighth of an inch in diameter were sealed in at the opposite sides of the bulb. Two lengths of wire, one of copper, Standard Wire Gauge 30, the other of constantin, Standard Wire Gauge 33, were joined with hard solder, and inserted through the side tubes so that the join of the two wires occupied the foot of the tube in the bulb. Copper and constantin were chosen since they could be easily obtained, and gave a large E.M.F. for small changes of temperature. With the wires in this position the ends of the side tubes were heated and drawn off so that the glass collapsed on to the wire, and effected a complete seal. In spite of expectations to the contrary, no trouble was experienced because of the difference in coefficient of expansion between the metal and the glass. None of the tubes used broke from this cause. The wires were bent back from the point where they emerged from the side tube, and given a number of turns round the glass, so that the strain of continual bending just at the point of emergence from the glass seal was reduced, and the "life" of the tube prolonged /

prolonged. A glass stopper was ground into the mouth of the tube.

A diagram of the tube follows:-



THE THERMOCOUPLE.

The junction of the copper and constantin wires inside the tube, in all cases except pinene, acted as the hot junction of the thermocouple. A similar join of two other pieces of the copper and constantin wires was made, and placed in a suitable holder /

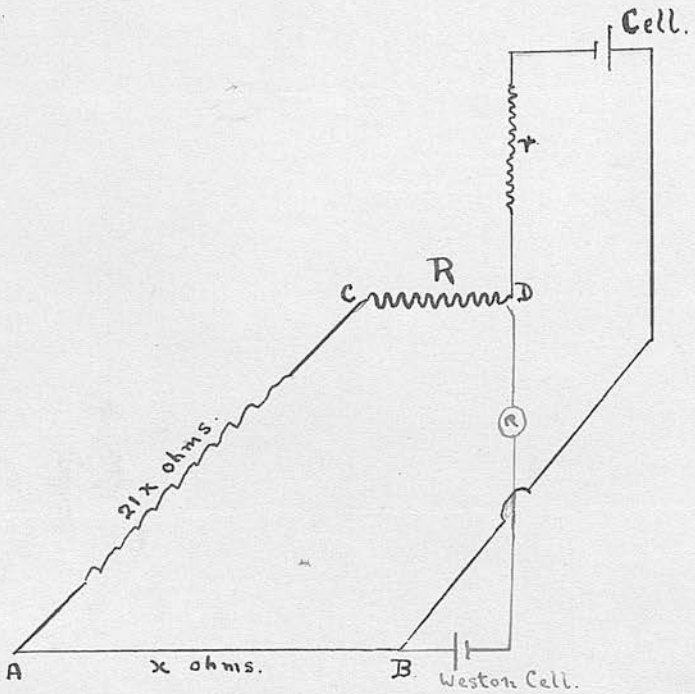


Fig 1.

holder to form the cold junction. The temperature was kept steady at $0^{\circ}C$. for several hours by immersing this junction in an "ice-mush" in a test tube, which was placed in a vacuum vessel filled with ice and water. This "ice-mush" was obtained by freezing distilled water, and cutting down the piece of ice so formed with a razor blade. In the actual experiments the constantin wires from the two junctions were twisted together, the join being kept in ice, while the copper wires from both junctions were led to the potentiometer.

THE POTENTIOMETER.

This instrument was made by Cambridge and Paul. Twenty one bobbins each of the same resistance as the bridge wire are arranged in series. In this way a considerable range of E.M.F. can be accurately measured. The instrument was altered somewhat in order to be able to read accurately very small voltages, such as would be encountered throughout the experiments.

The general plan of the apparatus is shown diagrammatically in Fig. I. AB is the bridge wire of resistance x ohms, AC contains the twenty /

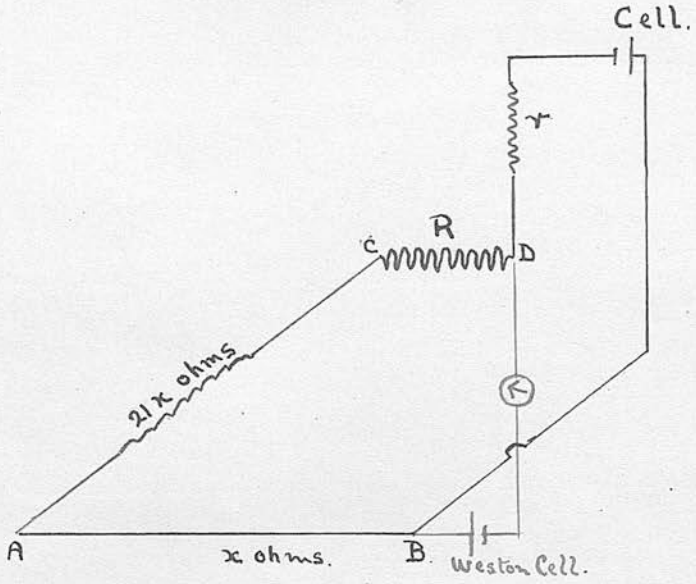

Cell.
r
R
C
D
21 x ohms
A
x ohms.
B.
Weston Cell.

Fig. 1.

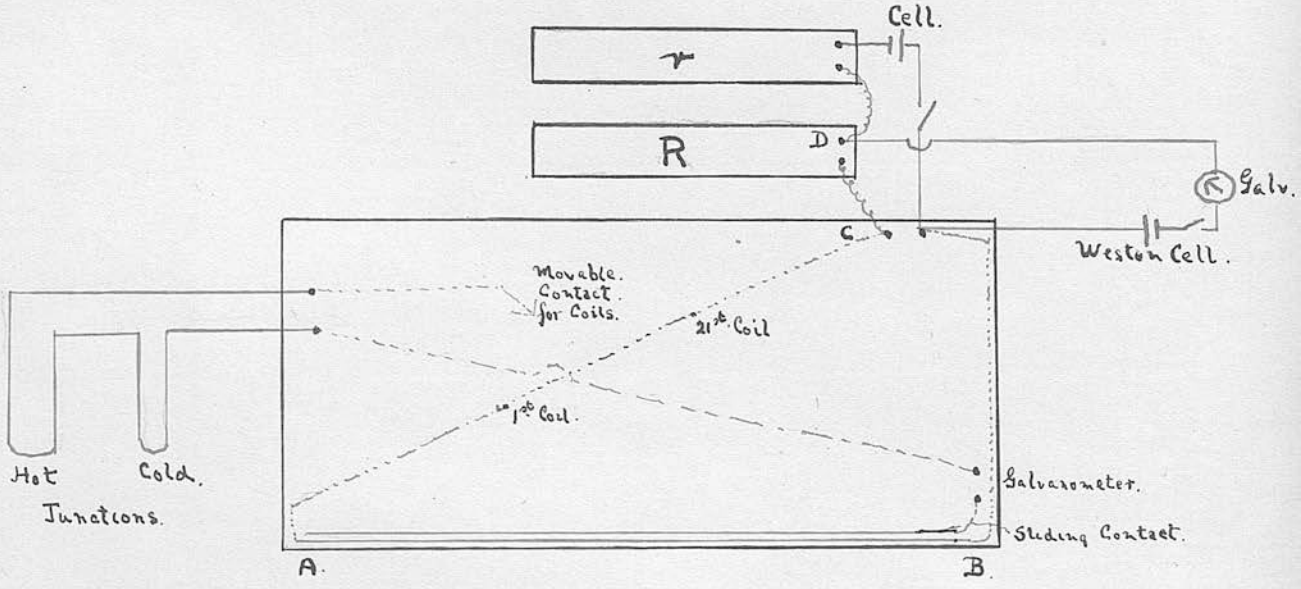

Cell.
r
R
D
Galv.
C
Weston Cell.
Movable Contact for Coils.
21st Coil
1st Coil.
Hot Junctions.
Cold.
Galvanometer.
Sliding Contact.
A.
B.

Fig. 2.

twenty one coils each of resistance x ohms, and R is a large resistance placed between C and D. For the purpose of this explanation BACD can be looked upon as the actual "Bridge". To the ends of this bridge an accumulator is connected, but in this circuit a resistance r is interposed, which is of such a magnitude as to reduce the voltage between B and D from 2.2 v. to 1.019 v.. In order to find the value of r, a Weston cell with a galvanometer in circuit is connected to B and D. r is then adjusted so that no deflection is shown in the galvanometer. In this way by frequent testing with the Weston cell a constant fall of potential between B and D was maintained. R was calculated so that

$$\frac{x}{R+22x} = \frac{1}{1019} \quad ; \quad \text{i.e. } R = 997x.$$

i.e. so that the bridge wire (and each of the coils) took 1/1019 of the total fall of potential. i.e. 1/1019 of 1.019 v. = 0.001 v.. Hence each large division of the bridge, which consisted of 100 half cms., represented 1×10^{-5} v., and each small division represented 1×10^{-6} v.. 22x was found experimentally to be 51 ohms, hence R = 2312 ohms. In this way a fall /

fall of potential of 22x.001v.=0.022v. was maintained between C and B.

The measurement of the EMF. of the thermocouple was accomplished as shown in Fig. 2, where the actual potentiometer is represented, the dotted lines in red indicating wires in the interior of the instrument. From the fall of potential in the coils and the bridge wire, a sufficient amount was tapped off equal to the E.M.F. developed by the thermocouple, the point of balance being found on a very sensitive galvanometer connected to the terminals shown in the diagram. Accuracy in reading to $1x10^{-5}$v. was obtained with this instrument.

CONVERSION TO DEGREES CENTIGRADE.

The relationship between the E.M.F. of the thermocouple and the actual difference of temperature between the junctions is not absolutely linear, but for small ranges of temperature the error introduced by regarding it as such is negligible. In general then for each curve, two substances were chosen which melted at steady temperatures, one at either end of the range of the melting point curve. These /

These melting points were found

(a) with each thermocouple

(b) with an accurate Thermometer.

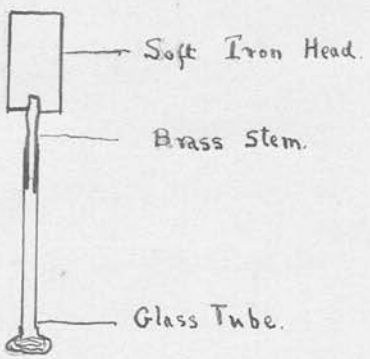
This thermometer was corrected for emergent stem, and compared with a standard thermometer. Hence two fixed temperatures were expressed as bridge readings for each thermocouple, and from these a gradient calculated, which was valid for that range of temperature, and enabled E.M.F. measurements to be converted. In practice it was found that 100 divisions of the scale on the bridge did not correspond exactly to the resistance of one of the coils, but that 94 divisions had the same resistance. Hence all readings on the scale were increased by 6.4%. This, of course, did not apply to that portion of the E.M.F. measured by the coils. Owing to the high temperature employed in some of the curves, some variations were observed in the values obtained for the thermocouple in the early readings. Accordingly all tubes before calibration were kept for 24 hours at 150°to 200°C.. In this way more constant values for the temperature were obtained.

STIRRING /

STIRRING.

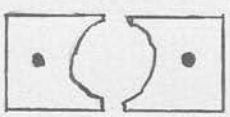
It was essential in all determinations to have effecient stirring. Two types of stirrer were employed. A was used when dealing with substances volatile at their melting points as, for example, borneol, when the determination had to be carried out in a tube completely closed; B was used for the remainder, as for example, pinene, when loss by volatilisation was negligible. In the case of type A, the stirring was accomplished by an electro megnetic stirrer.

Type A

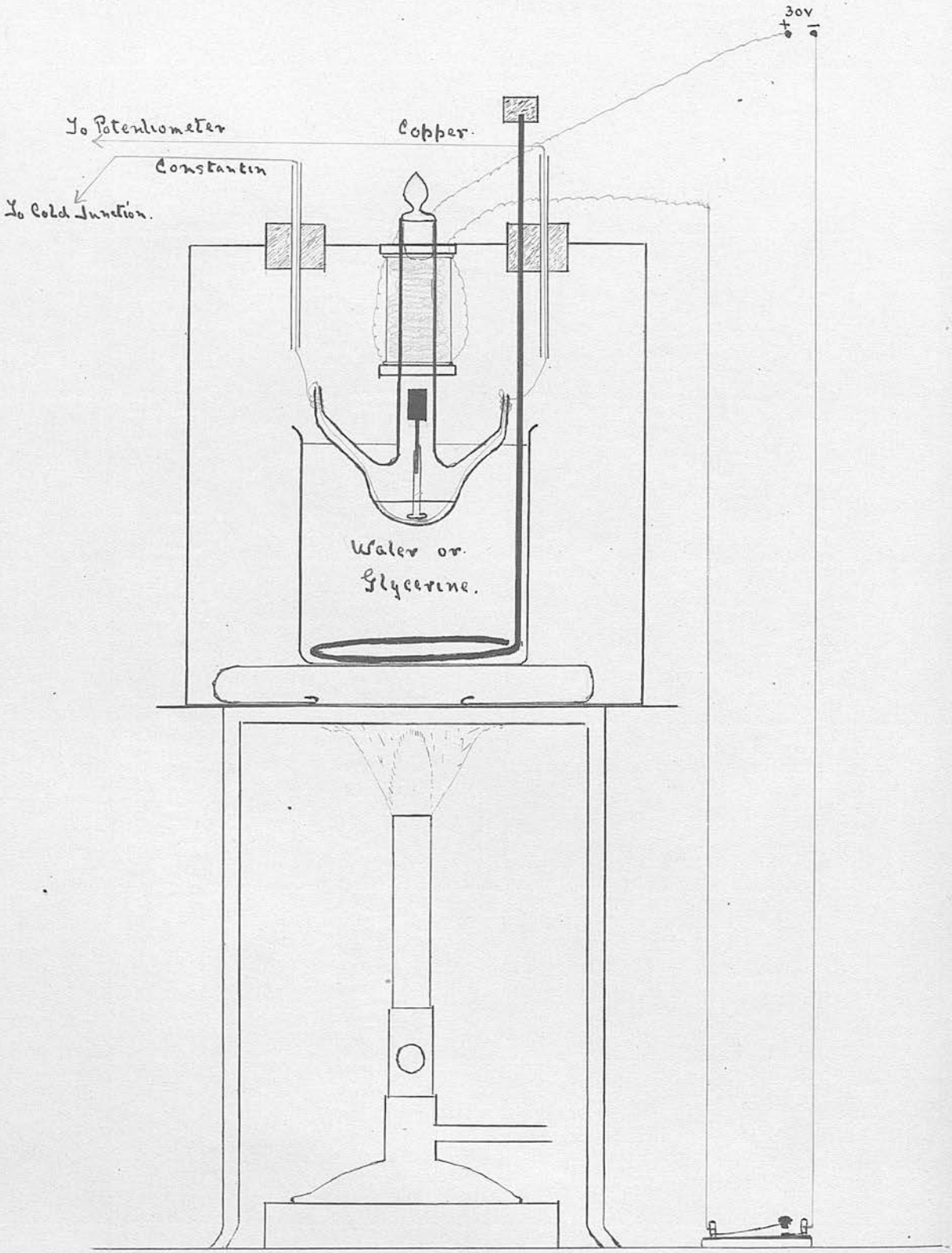


A small rod of soft iron half an inch long and a quarter of an inch in diameter was fitted with a short brass stem one inch long. A length of glass tubing was selected of internal diameter, such that the brass stem fitted it tightly; short lengths of from one and a half to two inches were cut, and a large blob of glass melted on the end /

end of each. For each experiment one of these was pushed on to the brass stem of the soft iron head; this was placed inside the tube, and constituted the internal portion of the stirring arrangement. Two small bobbins of five ohms. resistance, made of enamelled copper wire, were fitted with cores of soft iron and screwed on to a plate of the same material, which had a hole in the centre to allow of the passage of the top of the melting point tube. At the other end of the bobbins two pieces of soft iron were screwed in to act as a magnetic poles, and of such a shape that they fitted close to the tube. See diagram



All the determinations, which employed this type of stirring were carried out in a bath of glycerine or water, which was contained in an air oven fitted with a mica window at back and front, and illuminated from behind. The bobbins were screwed into, and so suspended from the top of this oven, and the melting point tube passed up through the middle, the final position being one in /


30V
+
−
To Potentiometer
Copper.
Constantin
To Cold Junction.
Water or
Glycerine.

in which the soft iron head of the stirrer was about half an inch below the lower end of the bobbin. The thermocouple wires were passed up through two holes in the roof of the oven in glass tubes held in position by corks. A potential of 30 volts was applied to the bobbins, contact being made and broken regularly when required by a tapping key in the circuit, which could be depressed by hand. The movement of the stirrer gave very effecient stirring, when setting points were being determined, and fairly good in the case of melting points.

Type B was a glass stirrer, simply a rod which had been flattened at one end to as wide a diameter as the melting point tube would allow. It moved inside a glass tube, and was worked by hand.

B O R N E O L.

The calibration of the thermocouples was carried out with

d-borneol	melting at	206.5°C
	and	
d-camphor	melting at	178.6°C

the temperature being measured on an Anschutz Thermometer, and corrected. A stirrer of type A was used in all experiments.

The heating was effected in a glycerine bath in the air oven. A large bunsen was employed in the earlier stages, but was replaced by an ordinary one when the temperature of melting was approached, and the latter turned out just before melting occurred. Air cooling prevented the temperature from rising much above the melting point. Great care had to be taken to prevent this occurring, since if kept at a temperature more than one degree above its melting point, borneol began to decompose, a brown mass being formed.

In attempting to get a melting point of the borneol, no definite point was obtainable, either as a steady point during the melting of the solid, or as the point where the last trace of solid disappeared.

Some /

Some indication was given, however, of the probable setting point which was accurately determined on cooling. A point was always found at which the temperature remained constant for a brief period of time, and in some cases the temperature rose to a steady value. The observance of this rise, which does not seem to have been generally noticed in the determination of such setting points, is probably due to the sensitiveness of the thermocouple to slight and momentary changes of temperature, compared with the comparatively slowly acting thermometer.

By taking due precautions to avoid overheating, it was possible to repeat the setting point of each mixture two or three times, but thereafter the temperature of solidification became lower and lower, and finally a brownish colour was developed. The tube had then to be cleaned out, dried, and a fresh sample employed. An accurate value for the setting point was only possible in the case of the purest samples of borneol. The mixtures used were prepared in a weighing bottle, and brushed into the tube with a camel hair brush, over a sheet of glazed paper. Very small quantities of the substances could /

could be employed, only about 0.3 to 0.5 grams being necessary.

As the tubes were heated up to about 200°C. from the ordinary temperature, a considerable pressure was developed inside the tube, and this was released just before the melting point was taken.

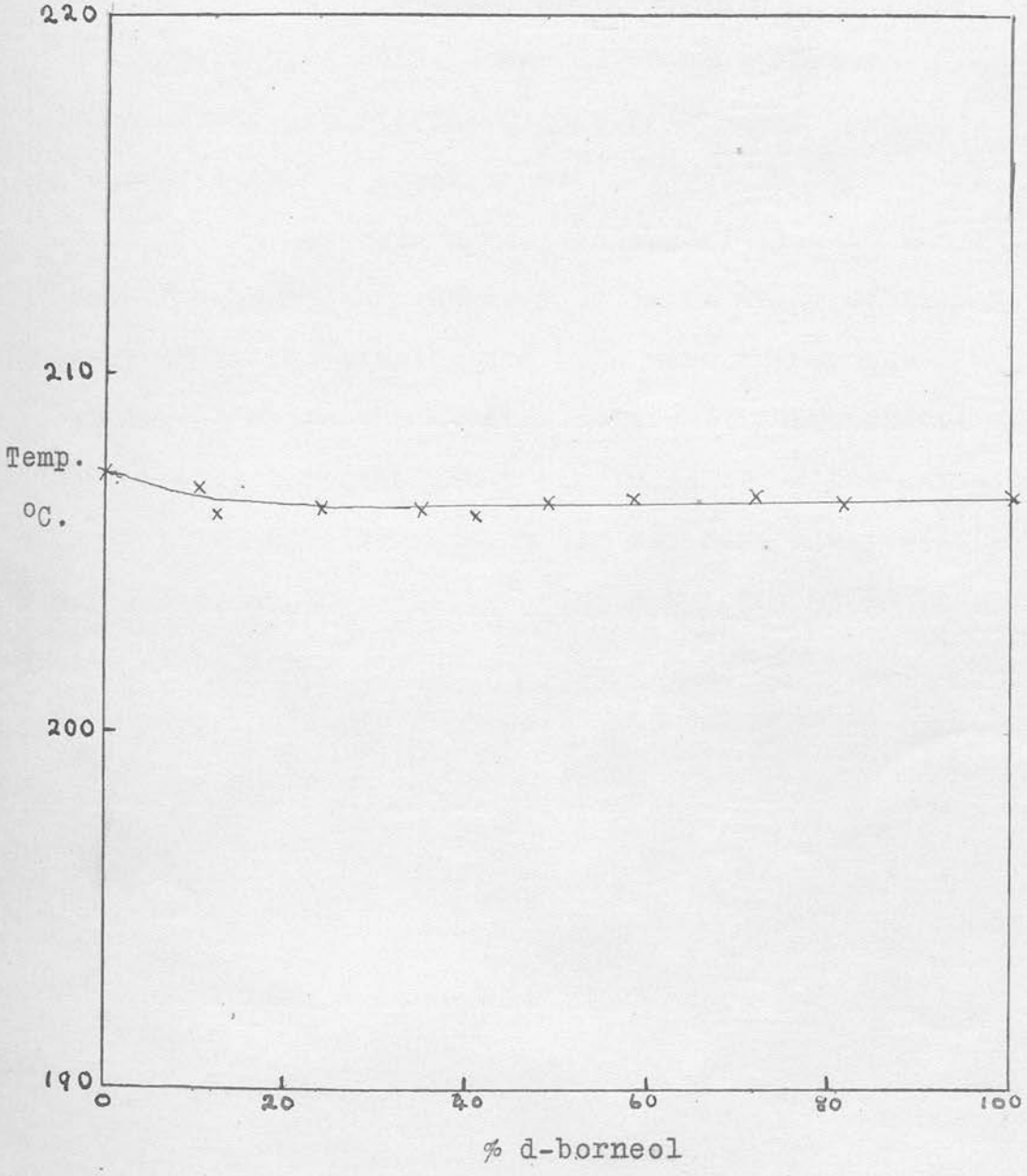
The table of results and corresponding curve are shown on pages 33-34.

DEXTRO and LAEVO BORNEOLS.

% d-borneol	Setting Point in °C
100.00	206.5
81.30	206.4
72.04	206.6
49.48	206.4
40.75	206.0
35.40	206.2
24.06	206.2
12.35	206.1
10.45	206.8
0.00	207.2

DEXTRO AND LAEVO BORNEOLS.

SETTING POINT CURVE



C A M P H O R.

The calibration of the thermocouples was carried out with

d-borneol	melting at	206.5°C
	and	
d-camphor	melting at	178.6°C

the temperatures being measured on an Anschutz Thermometer, and corrected. A stirrer of type A was used in all experiments.

The procedure was exactly similar to the case of d-borneol. Here, also, slow decomposition occurred if the temperature rose more than about one degree above the melting point. Each mixture served only to establish a single point on the curve.

The melting point did not give a satisfactory value, so the setting point was found as in the case of borneol.

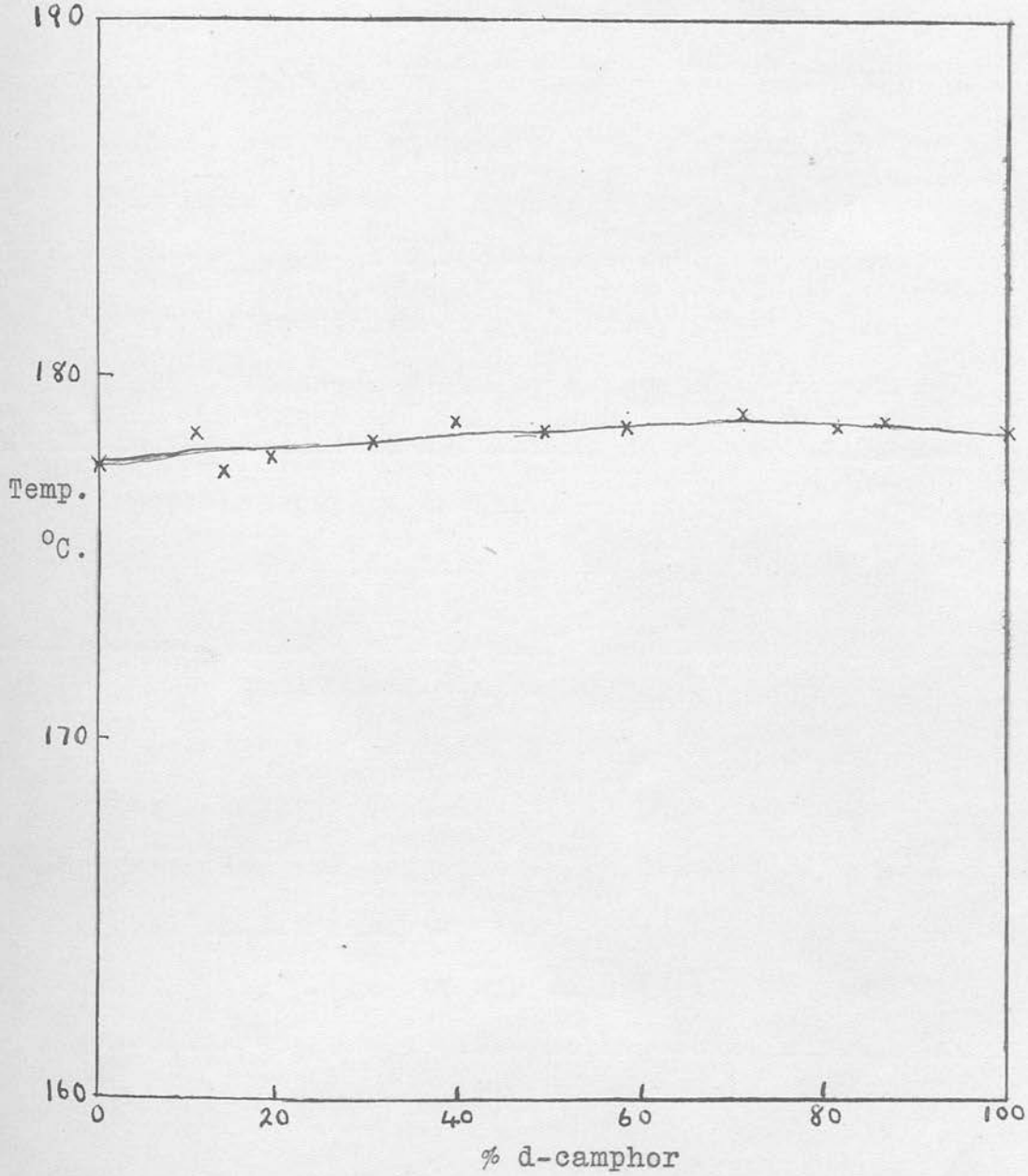
The table of results and corresponding curve are shown on pages 36-37.

DEXTRO and LAEVO CAMPHORS.

% d-camphor	Setting Point in °C
100.0	178.6
86.2	178.8
81.0	178.6
70.8	179.1
57.9	178.7
48.7	178.6
39.3	178.8
30.1	178.3
19.1	177.8
13.8	177.4
11.3	178.5
0.0	177.7

DEXTRO AND LAEVO CAMPHORS.

SETTING POINT CURVE.



DEXTRO BORNEOL and DEXTRO CAMPHOR.

This curve had already been worked out by Vanstone [J.C.S. 1909, 597]. The d-borneol which he employed was not pure, due to the presence of l-isoborneol. It melted at 208.6°C., and gave a rotation of $[\alpha]_D = +27.66^\circ$. Moreover, the experiment was not carried out in a closed tube, so that some loss by volatilisation was almost certain to occur. The temperature measurements, as given by the thermocouple, are probably more accurate than those given by Vanstone. Accordingly it was decided to re-determine the curve, using pure d-borneol and pure d-camphor.

The calibration of the thermocouple was carried out with

d-borneol melting at 206.5°C.
and
d-camphor melting at 178.6°C.

the temperatures being measured on an Anschutz Thermometer, and corrected. A stirrer of type A was used in all experiments.

The procedure was exactly the same as in the case of d-borneol, the setting point curve being worked out.

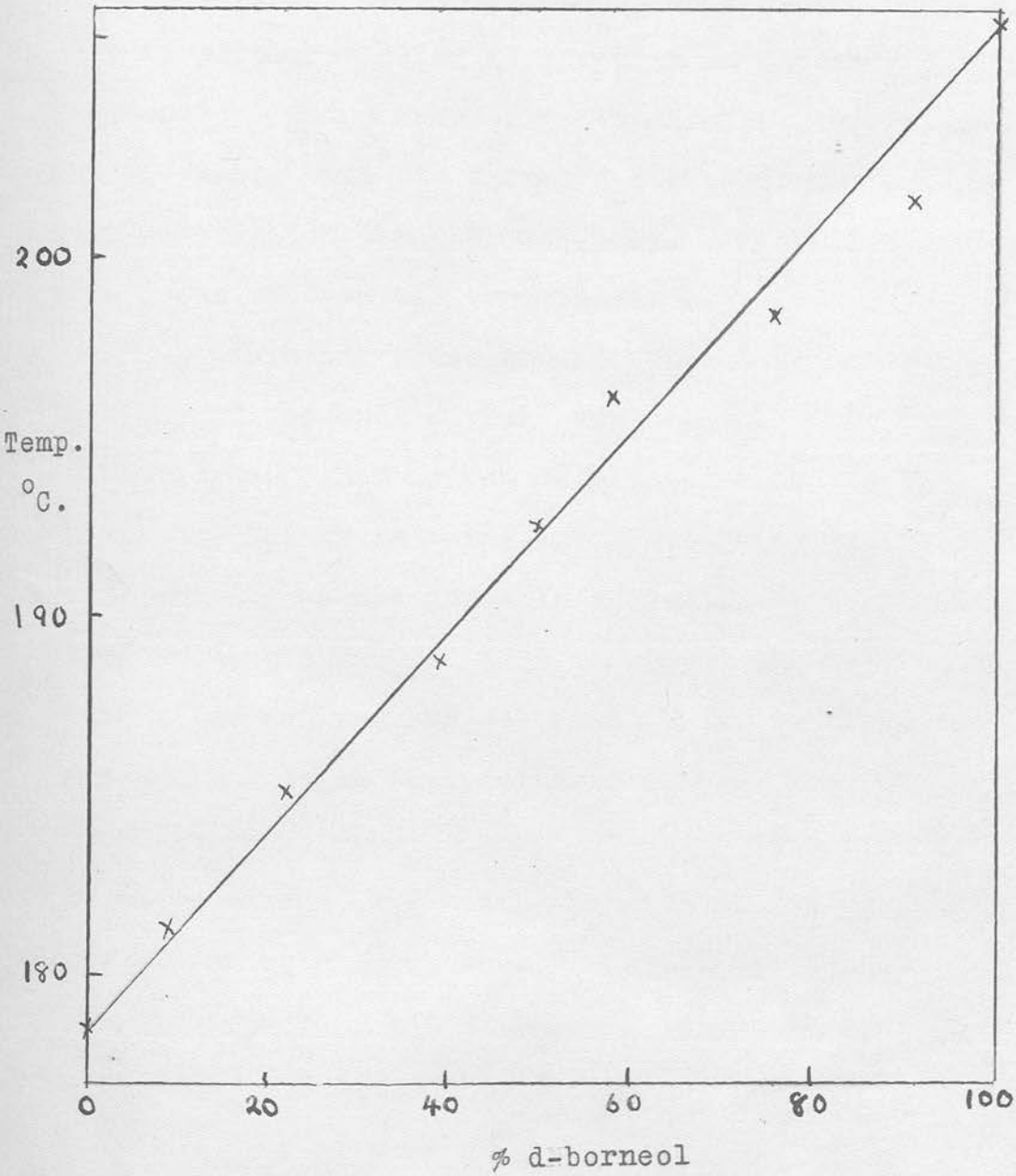
The table of results and corresponding curve are shown on pages 39-40.

DEXTRO BORNEOL and DEXTRO CAMPHOR.

% d-borneol	Setting Point in °C
100.0	206.5
90.4	201.7
75.7	198.5
57.3	196.2
49.0	192.7
37.8	188.9
21.3	185.3
8.4	181.4
0.0	178.6

DEXTRO BORNEOL AND DEXTRO CAMPHOR.

SETTING POINT CURVE.



C A M P H O R I C A C I D.

The calibration of the thermocouples was carried out with

d-borneol	melting at	206.5°C.
	and	
d-camphor	melting at	178.6°C.

the temperatures being measured on an Anschutz Thermometer, and corrected. Frequent recalibration was necessary owing to the slow action of the acid on the metals of the thermocouples. A stirrer of type A was used in all experiments.

This curve was more difficult to determine than any of the ones already dealt with. The camphoric acid when melted decomposed with great readiness, though in this case no charring was to be seen, and it was not possible to get a setting point after melting once, far less to repeat the melting point after cooling and reheating. It was therefore necessary to begin every mixture afresh, heat it up carefully, and take the point at which it melted for the first time. The mixing was not so good as when the setting point of a melted mixture was to be determined. The melting point obtained on heating was/

was indicated usually by a fall of temperature, followed by a brief steady interval, and then a further rise as the solid disappeared. This short steady interval was the point taken, as no steady value was observed when the last trace of solid disappeared.

The table of results and corresponding curve are shown on pages 43-44.

Equal quantities of d- and l- acids were accurately weighed out, mixed, and recrystallised together from aqueous alcohol. Racemic acid was obtained of melting point 202.6°C., rather over two degrees higher than that found in the curve for a 50% mixture of d- and l-. This difference is probably due to a certain amount of decomposition in the latter case. A melting point curve was found for mixtures of d- and r- acids, in exactly similar a way to the above d- and l- acids.

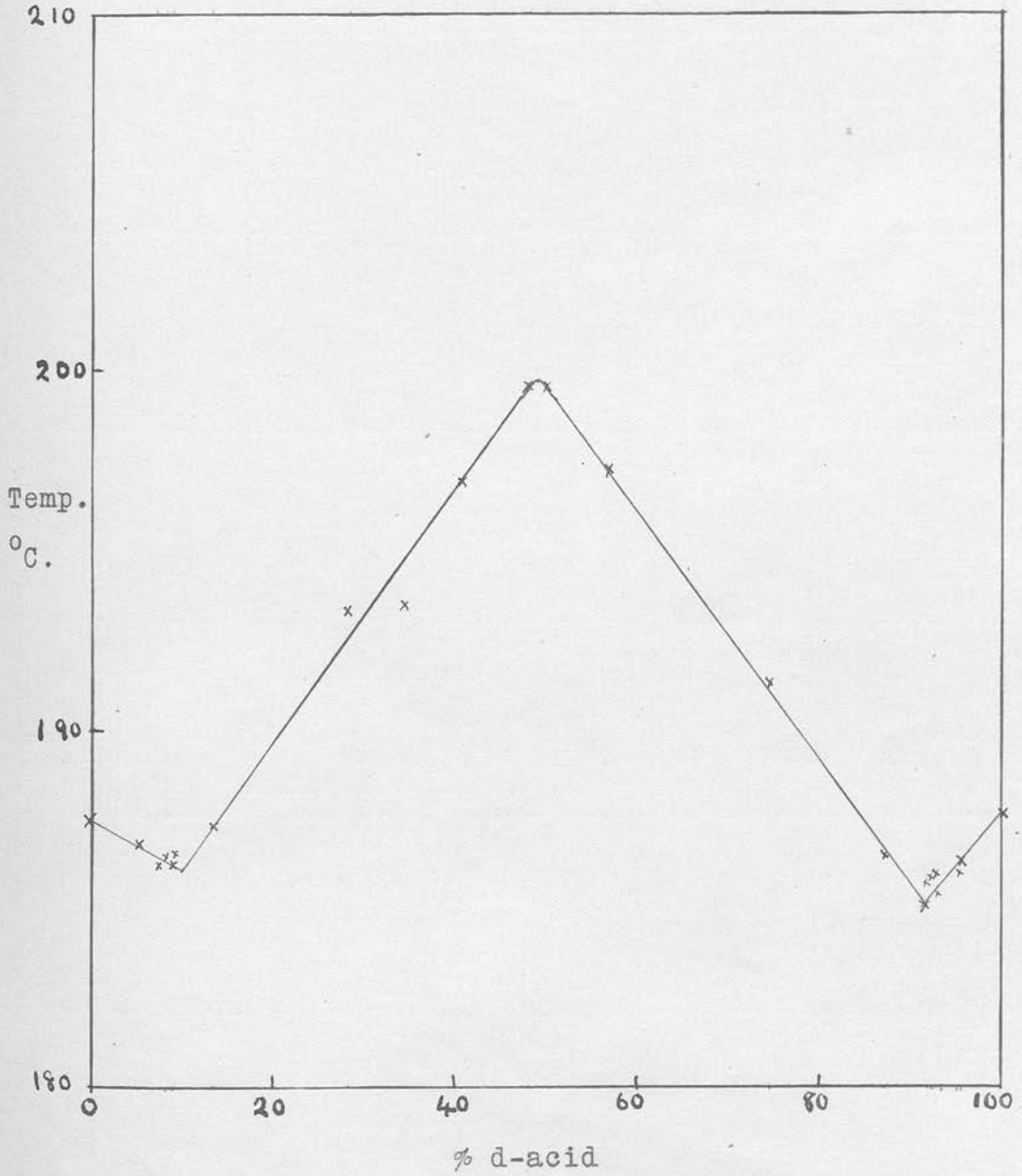
The table of results and corresponding curve are shown on pages 45-46.

DEXTRO and LAEVO CAMPHORIC ACIDS.

% d-acid	M.P.in °C	% d-acid	M.P.in °C
100.00	187.6	49.83	199.5
95.40	185.9	47.86	199.6
95.10	186.3	40.70	196.9
93.47	185.4	34.43	193.4
92.70	185.9	28.10	193.3
92.30	185.8	13.40	187.3
92.26	185.2	8.87	186.7
92.15	185.8	8.43	186.3
92.10	185.0	8.03	186.5
91.80	185.0	7.35	186.2
87.30	186.5	5.47	186.8
74.40	191.3	0.00	187.5
56.94	197.2		

DEXTRO AND LAEVO CAMPHORIC ACIDS

MELTING POINT CURVE

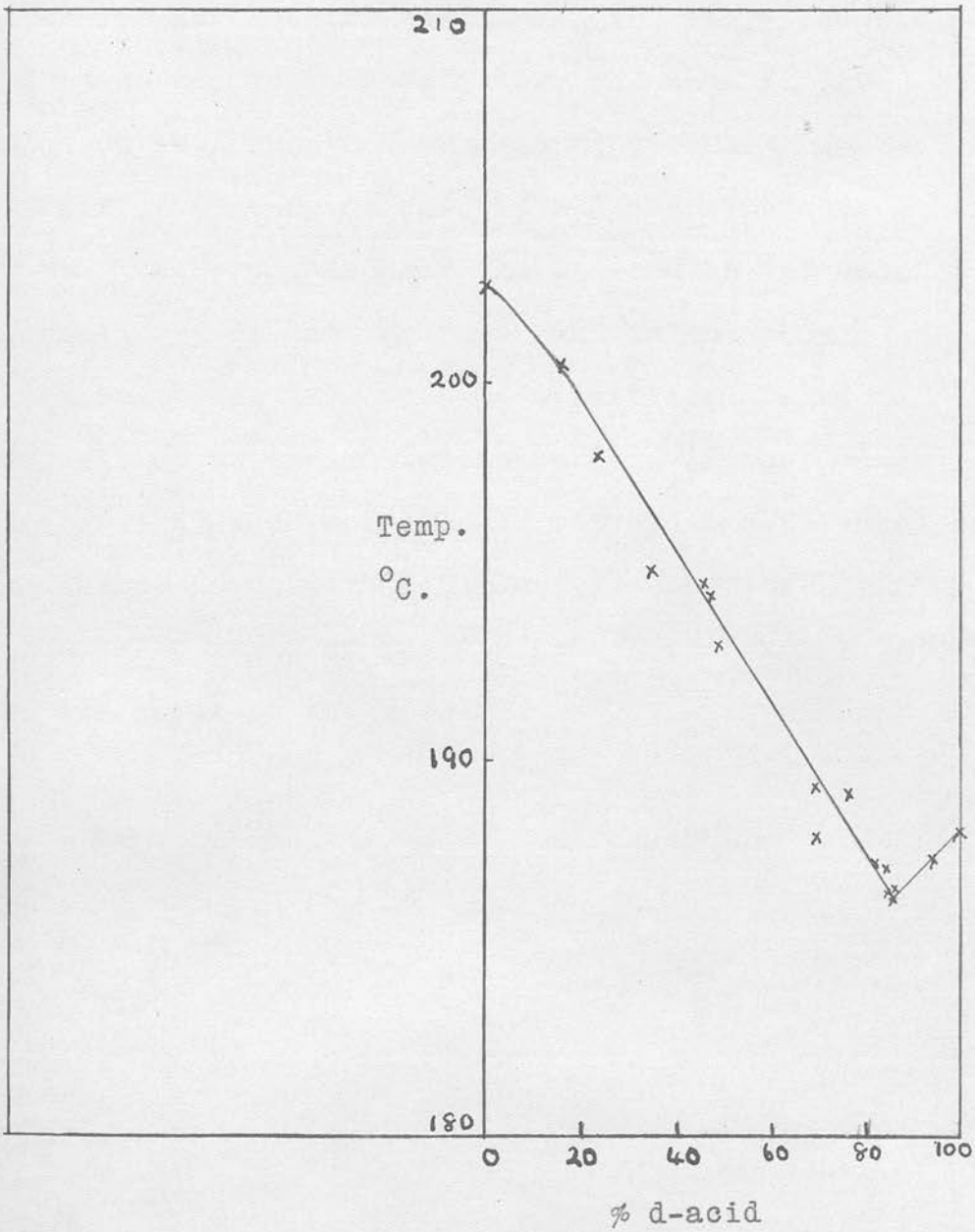


DEXTRO and RACEMIC CAMPHORIC ACIDS.

% d-camphoric acid	Melting Point in °C
100.00	188.2
93.48	187.3
85.70	186.5
85.40	186.4
84.17	186.5
84.04	187.1
81.72	187.2
75.57	189.1
69.62	187.9
69.38	189.3
49.17	193.1
46.91	194.5
45.77	194.7
36.39	197.1
35.19	195.1
23.63	198.1
16.01	200.5
0.00	202.6

DEXTRO AND RACEMIC CAMPHORIC ACIDS.

MELTING POINT CURVE



CAMPHORIC ANHYDRIDE.

The calibration of the thermocouples was carried out with

d-camphoric anhydride	melting at	223.8°C.
	and	
d-borneol	melting at	206.5°C.

The temperature of the melting of the anhydride was found on an accurate thermometer, and that of the borneol on an Anschutz Thermometer; both were corrected. A stirrer of type A was used in all experiments.

The procedure was the same as in the case of borneol. The setting point was taken, though the melting point gave an almost identical value. Decomposition of the melted anhydride, if any, was very slow, and each point could be repeated several times, and so found with considerable accuracy.

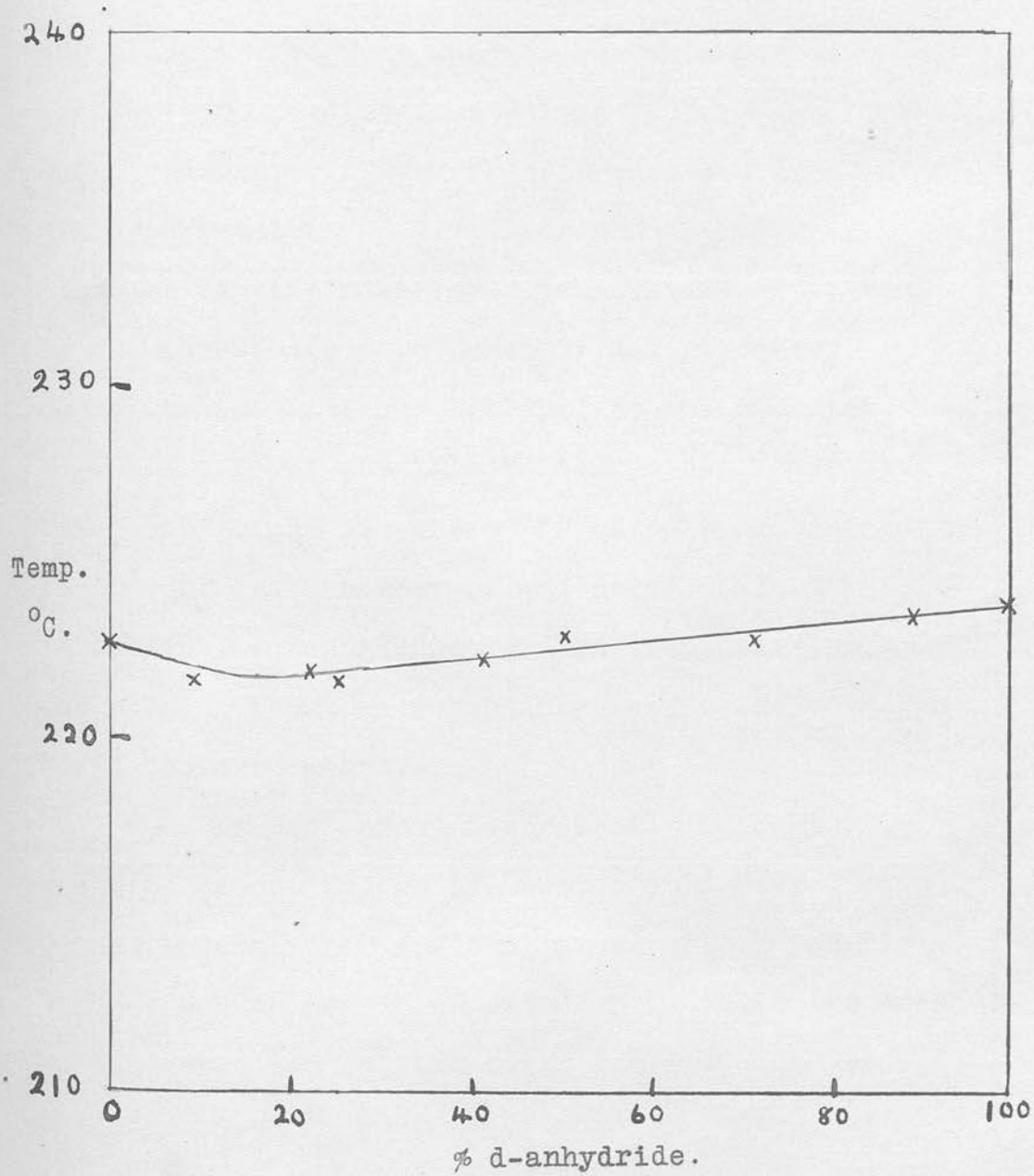
The table of results and corresponding curve are shown on pages 48-49.

DEXTRO and LAEVO CAMPHORIC ANHYDRIDES.

% d-camphoric acid anhydrides	Setting Point in °C
100.00	223.8
88.80	223.5
71.62	222.8
50.24	222.9
41.37	222.2
25.00	221.6
22.14	221.9
9.43	221.7
0.00	222.9

DEXTRO AND LAEVO CAMPHORIC ANHYDRIDES.

SETTING POINT CURVE.



ORTHO METHYL CAMPHORIC ESTER.

The calibration of the thermocouples was carried out with

dinitrobenzene	melting at	90.50°C.
	and	
diphenyl	melting at	68.70°C.

The temperatures were measured on an accurate thermometer, reading from 50° to 100°C., in 1/10ths. and corrected. A stirrer of type B was used in all experiments.

At the much lower temperature of melting of the ester, a closed tube was not necessary. The glycerine bath was replaced by one of water. It was not found possible to determine a setting point curve, not because of decomposition, but on account of the tendency of the ester to form an oil on cooling. Repeated determinations, however, of the melting point were possible, and these were found for each mixture.

In the actual experiment a weighed quantity of one of the isomers, say, d-ester, was placed in the tube, and the latter put in position. The water bath was then heated up. As in the case of the acid, the melting point was indicated by a slight /

slight fall of temperature, a brief steady interval, followed by a more rapid rise as the solid disappeared. As soon as the steady interval was completed, the hot water of the bath was syphoned off and replaced by cold. In this way the time of solidification was shortened. If the ordinary rate of cooling was adhered to, the ester remained as an oil for some considerable time. This determination of the melting point was repeated two or three times, or until constant results were obtained. A quantity of the l-ester was then added to the tube in situ, and the melting point of the mixture found. A further quantity of the l-ester was added thereafter, and so on, until the whole curve was completed. Confirmatory results were obtained by starting with the pure l-ester.

The table of results and corresponding curve are shown on pages 52-53.

In the course of the preparation of the l-ester, some became racemised. This was used to find a melting point curve for d-and r-ester. The procedure was exactly the same as above.

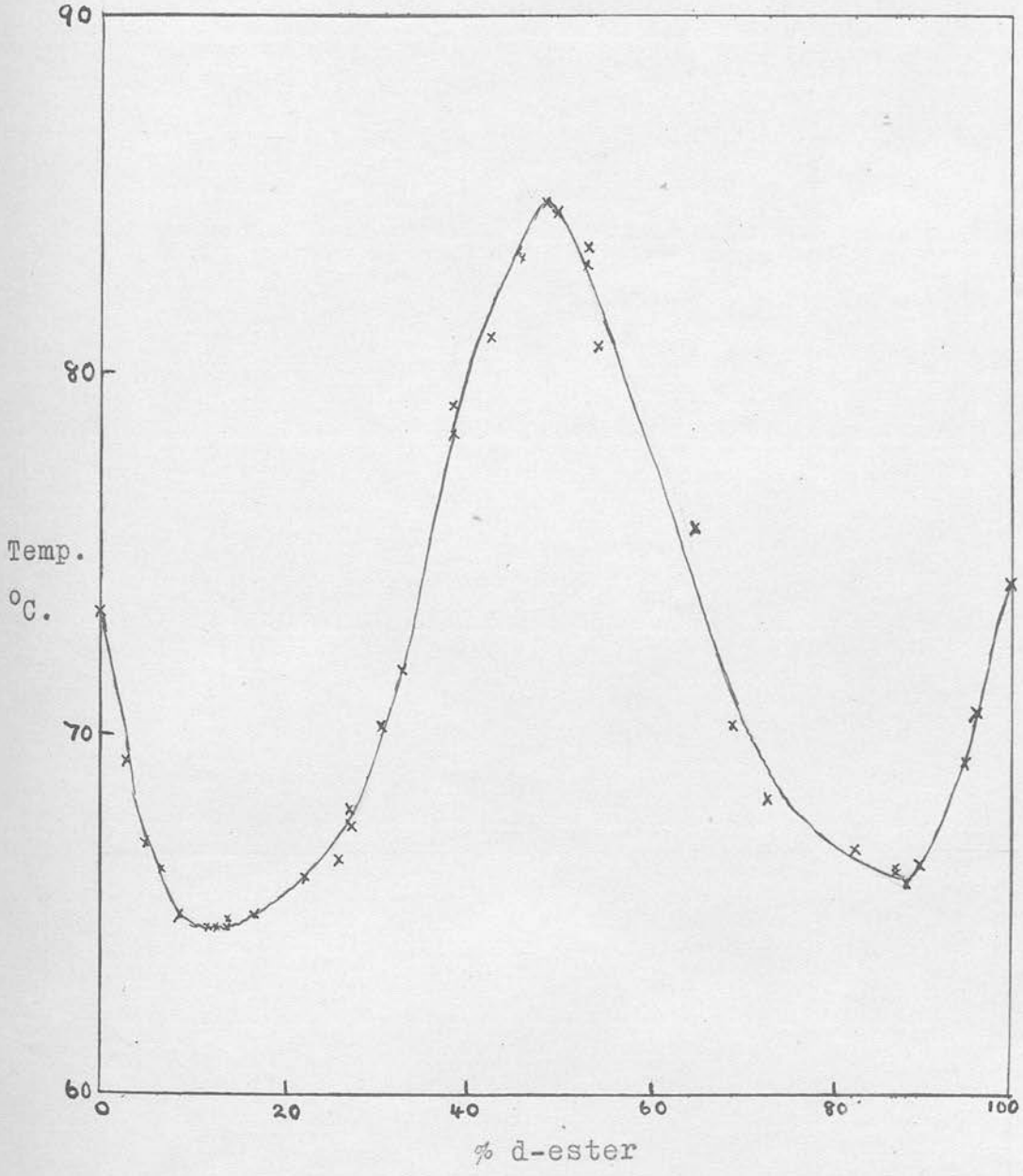
The table of results and corresponding curve are shown on pages 54-55.

DEXTRO and LAEVO METHYL CAMPHORIC ESTERS.

% d-ester	M.P.in °C	% d-ester	M.P.in °C
100.00	74.3	38.43	79.1
95.58	70.8	38.39	78.3
89.65	66.5	33.30	71.9
88.00	65.9	30.71	70.4
87.40	66.2	27.42	67.4
86.90	66.4	27.18	67.9
82.20	66.9	25.84	66.5
73.24	68.3	22.55	66.1
69.50	70.3	17.00	65.0
64.58	75.9	14.34	64.8
53.85	83.6	14.10	64.7
53.45	83.1	13.38	64.7
49.86	84.6	12.00	64.6
48.63	84.8	9.39	65.0
45.96	83.4	6.19	66.3
45.66	83.4	4.79	67.1
42.43	81.0	2.52	69.3
		0.00	73.5

DEXTRO AND LAEVO METHYL CAMPHORIC ESTERS.

MELTING POINT CURVE.

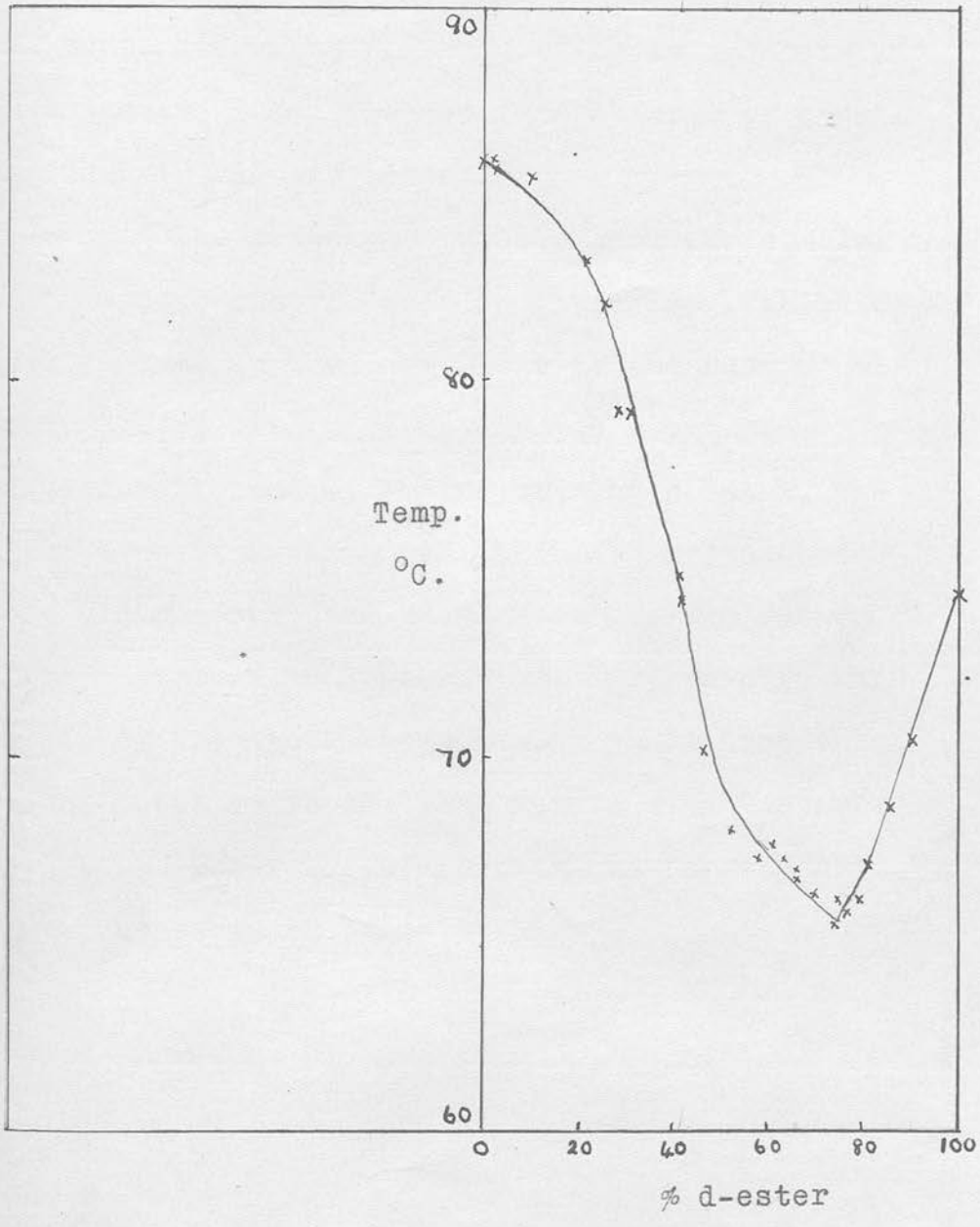


DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

% d-ester	M.P.in °C	% d-ester	M.P.in °C
100.00	74.4	58.00	67.2
90.28	70.5	51.61	68.0
85.10	68.7	46.5½	70.2
80.04	67.0	41.53	74.2
78.94	66.2	41.29	74.8
75.81	65.9	33.32	79.2
74.28	66.2	26.01	82.2
73.08	65.6	22.56	83.3
69.54	66.3	9.90	85.5
66.58	67.0	1.43	85.7
66.18	66.6	1.41	85.9
63.05	67.3	0.00	85.9
60.24	67.6		

DEXTRO AND RACEMIC METHYL CAMPHORIC ESTERS.

MELTING POINT CURVE.



BORNYL HYDROGEN PHTHALATE.

The calibration of the thermocouples was carried out with

d-camphor melting at 178.6°C.

and

d-bornyl hydrogen phthalate melting at 161.4°C.

the temperatures being measured on an Anschutz Thermometer, and corrected. A stirrer of type A was used in all experiments.

The procedure in this case was similar to that of camphoric acid, a glycerine bath being used to heat up the tube. As in the case of the acid, decomposition of the melted substance occured very readily. The melting point at the first time of heating was taken. The tube was then cleaned out, and used in the determination of a fresh mixture. Somewhat variable results were obtained, but their range was so small that there was no doubt as to the real nature of the curve.

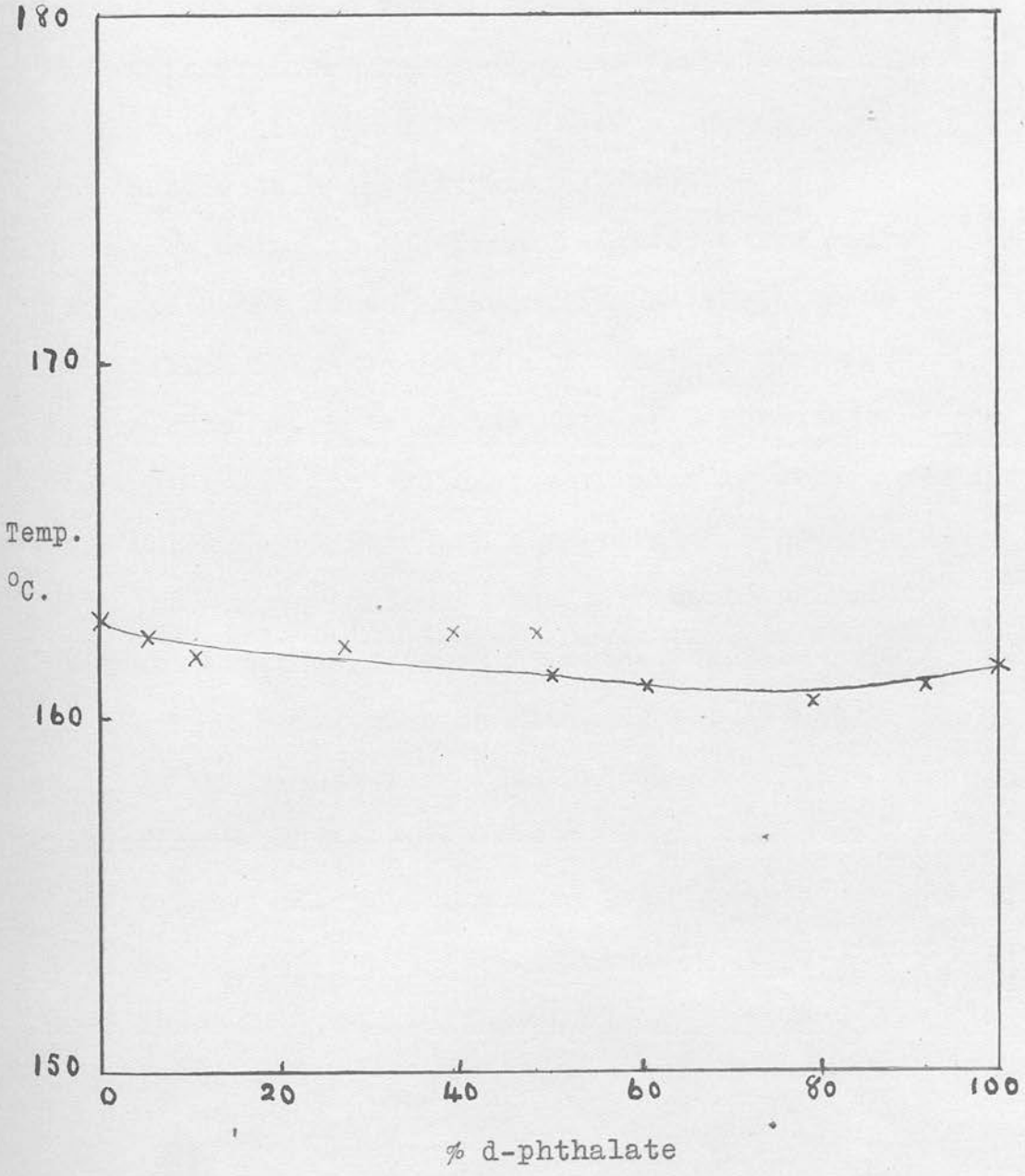
The table of results and corresponding curve are shown on pages 57-58.

DEXTRO and LAEVO BORNYL HYDROGEN PHTHALATES.

% d-phthalate	Melting Point in °C
100.00	161.4
91.60	160.8
78.90	160.5
60.00	169.9
49.65	161.1
48.08	162.5
38.55	162.5
27.00	162.1
9.74	161.7
5.27	162.3
0.00	162.8

DEXTRO AND LAEVO BORNYL HYDROGEN PHTHALATES

MELTING POINT CURVE



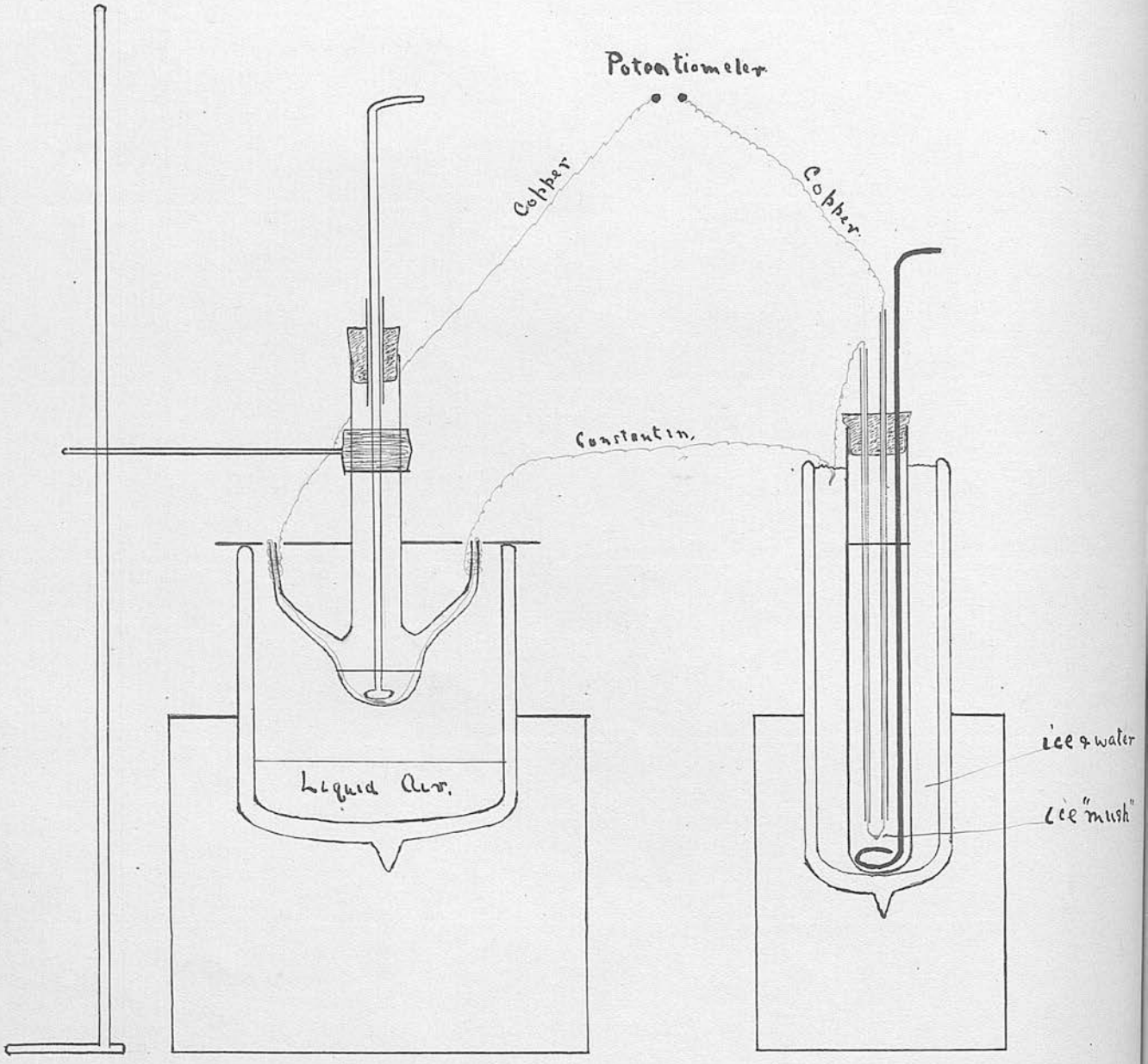
P I N E N E.

The low temperature necessary for the determination of this curve was obtained by immersing the tube in a bath of liquid air, contained in a vacuum vessel. The junction in the ice-water mixture thus became the "hot" junction, so that the direction of the flow of current in the thermocouple circuit was reversed.

Owing to the large range of temperature over which the curve extends, the calibration of the thermocouples was more difficult. Further, no accurate thermometer was available for those temperatures. Accordingly several pure substances were taken, and their freezing points determined with the thermocouples. The corresponding values of temperature were taken from the freezing points of the pure substances as given in the latest edition of Landolt-Bornstein Tabellen. The following were chosen:-

Diethylaniline	freezing point	- 38.1°C
Chloroform	freezing point	- 63.3°C
Toluene	freezing point	- 94.5°C
Ethyl Alcohol	freezing point	-114.2°C

The /


Potentiometer
Copper
Copper
Constantin
Liquid Air.
Ice & water
Ice "mush"

The relationship between the E.M.F. of the thermocouple and the temperature difference could not be assumed to be a linear one for this large range of temperature without considerable error. The gradient of the thermocouple decreased continuously over the range. From the values obtained with the above substances, a series of values of the gradient for every ten degrees range of temperature was calculated. These were used in converting the bridge readings into degrees Centigrade. A stirrer of type B was used in all experiments.

The freezing point of pinene was first tried in a bath of solid carbon dioxide and alcohol, but no definite point could be obtained owing to the extreme supercooling of the pinene.

The method finally adopted to measure the melting point was as follows:-

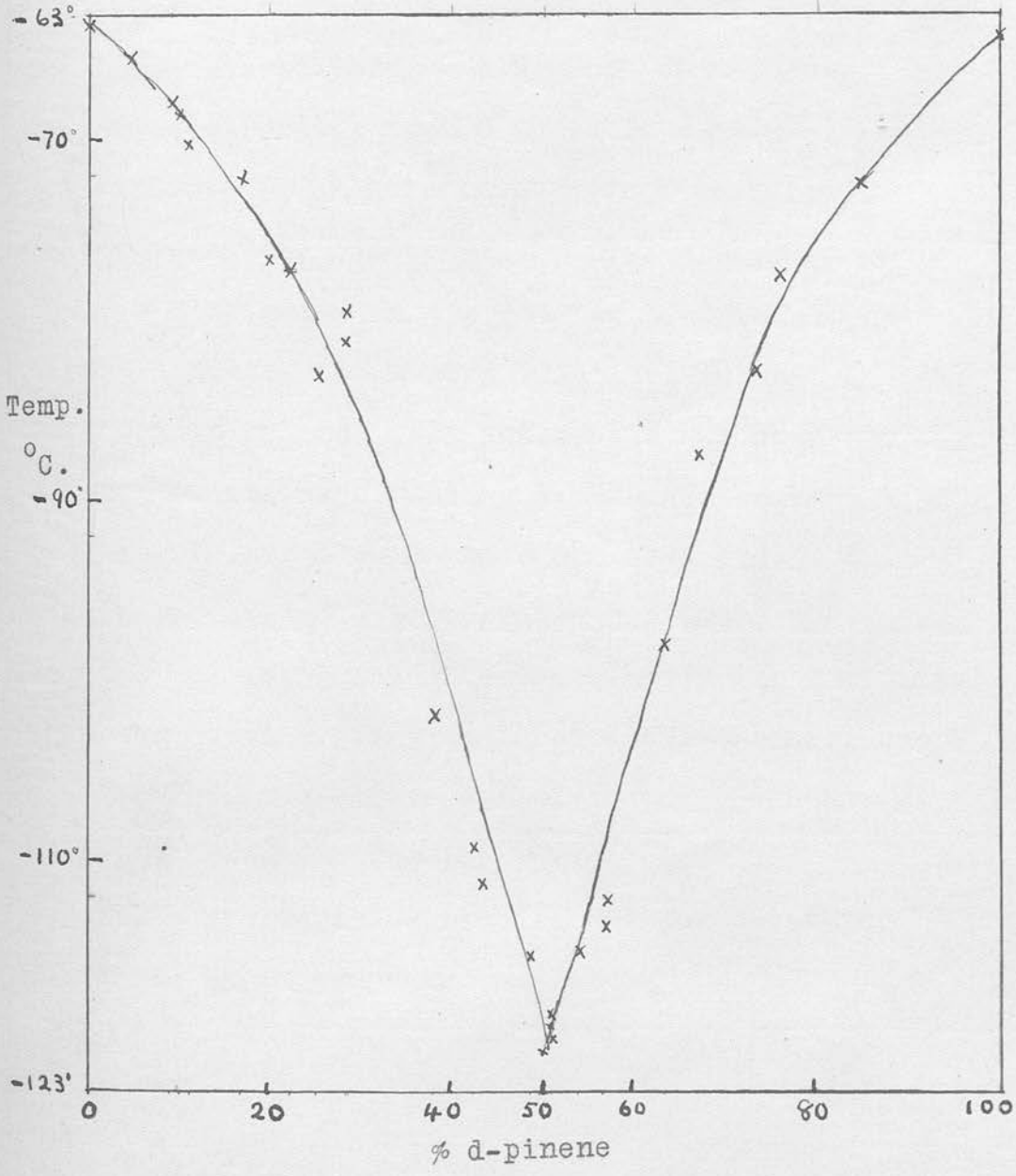
A weighed quantity of one of the isomers, say, d-pinene, was introduced from a weighing pipette into the tube, and the latter set in position in the vacuum vessel, which contained liquid air to the depth of about one inch. The stirrer /

DEXTRO and LAEVO PINENES.

% d-pinene	M.P.in °C	% d-pinene	M.P.in °C
100.00	- 64.1	43.30	-111.3
84.49	- 72.5	42.34	-109.5
75.78	- 77.7	38.09	-101.9
73.66	- 82.8	28.85	- 79.6
67.12	- 87.7	28.84	- 81.2
63.57	- 98.1	25.44	- 83.2
56.72	-112.4	22.17	- 77.1
56.58	-113.8	20.14	- 76.7
53.99	-115.1	16.92	- 72.2
50.65	-120.2	11.46	- 70.3
50.60	-118.7	10.21	- 68.8
50.36	-119.3	9.36	- 68.0
49.45	-120.8	4.95	- 65.4
48.50	-115.4	0.00	- 63.1

DEXTRO AND LAEVO PINENES.

MELTING POINT CURVE.



C A M P H E N E.

The calibration of the thermocouples was carried out with

Urethane	setting point	47.75°C.
	and	
Salol	setting point	41.64°C.

the temperatures being measured on an accurate thermometer reading from 0°C. to 50°C. in 1/10ths., and corrected. A stirrer of type A was used in all experiments.

In spite of the low temperature at which camphene melts, it is very volatile, so that a closed tube had to be used. A water bath was used for heating in the oven, and no decomposition of the camphene in the liquid state was observed. The setting point could be repeated a great many times, and the melting point gave practically the same value. When the setting point had been determined for one of the isomers, successive quantities of the other were added to it, and hence the curve completed.

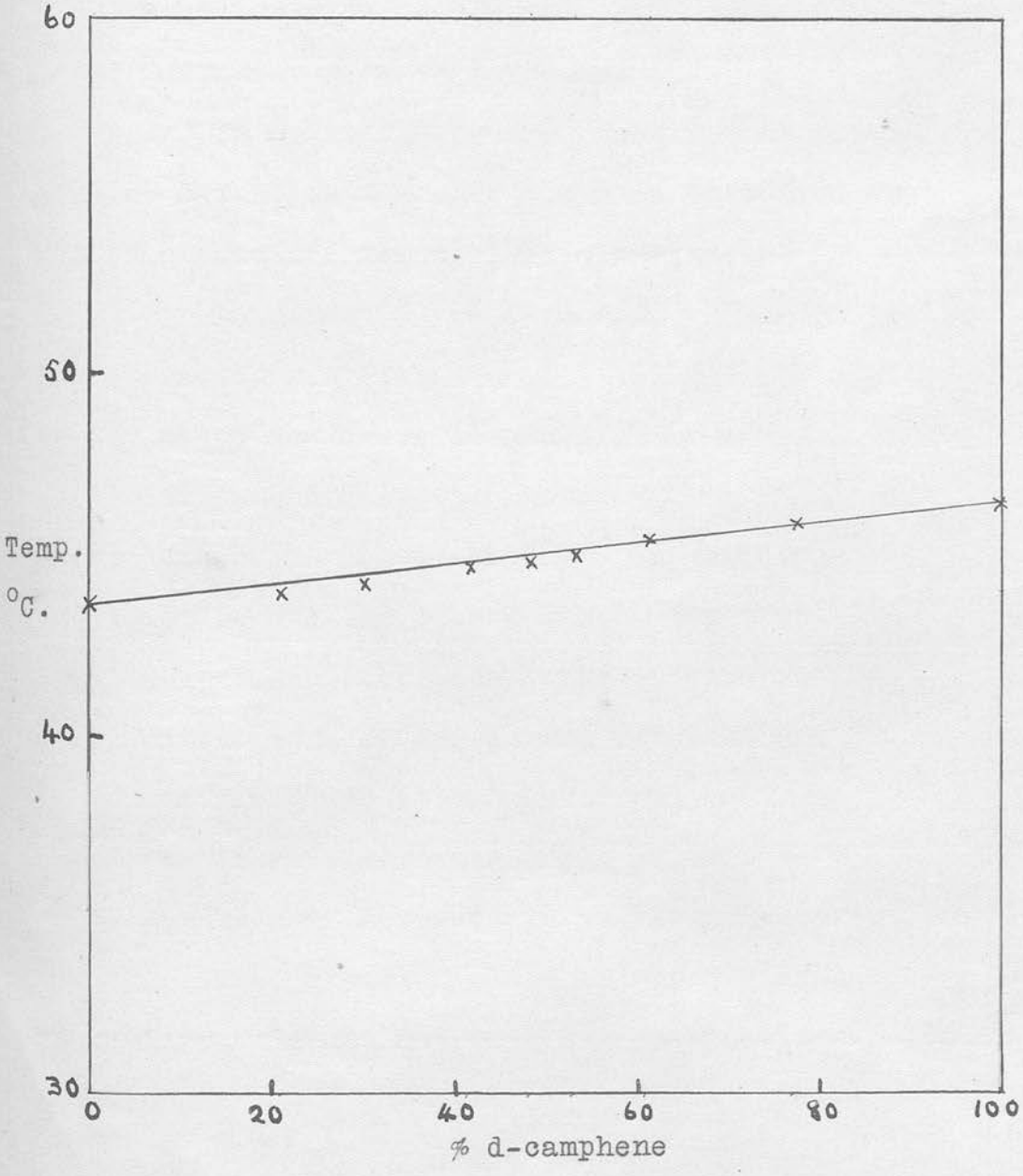
The table of results and corresponding curve are shown on pages 66-67.

DEXTRO and LAEVO CAMPHENES.

% d-camphene	Setting Point in °C
100.00	46.5
77.20	46.0
60.55	45.4
52.86	45.0
48.02	44.8
41.55	44.6
29.79	44.2
20.72	43.9
0.00	43.7

DEXTRO AND LAEVO CAMPHENES.

SETTING POINT CURVE.



ANALYSIS of EXPERIMENTAL CURVES.

The curves obtained fall into the three classes, described by Roozeboom.

(1) Curve for simple mixture d- and l-.

(2) Mixed Crystal curve.

(3) Curve for racemic compound.

In class (1) is the curve for d- and l- pinene, and it is the only curve of this kind that has been obtained for two optical isomers.

In class (2) we find most of the substances investigated, viz.,

(a) dextro and laevo borneols

(b) dextro and laevo camphors

(c) dextro and laevo camphoric anhydrides

(d) dextro and laevo bornyl hydrogen phthalates

(e) dextro and laevo camphenes

(f) dextro borneol and dextro camphor

In class (3) we have

(a) dextro and laevo camphoric acids

(b) dextro and laevo methyl camphoric esters.

The curves of class (2) do not lend themselves to exact mathematical examination. The equation /

equation, which they follow, has been worked out by Van Laar [Zeit. Phys. Chem. vol. 66], and is, of course, of the simple form $T = T_0 =$ constant, i.e. the curve should be a straight line joining the melting points of the pure d- and the pure l-, and should be at right angles to the temperature axis. All the curves found have this general form. Since the dextro and laevo isomers may form mixed crystals with each other, and the racemate, if formed, may also give mixed crystals with the dextro and laevo isomers, it is evident that this type of melting point curve does not give a definite answer to the question as to whether a racemic compound was formed or not. Tammann has investigated this question [Zeit. Phys. Chem. 87, 357], and by calculating the value of the quotient of the latent heat and the absolute temperature of melting, i.e. l_a/T_{oa} for the pure isomers, and for the 50% mixture of the isomers, he concludes that evidence may be found as to whether he is dealing with a racemate or a pseudoracemate. The assumption on which this is based is that the pure d- and l- isomers consist of single molecules. The same criterion, which Tammann takes /

takes as the evidence of the formation of a racemate, may be applied to the pure d- and l- isomers to determine whether or not they are associated. In the case of the pure isomers, we are dealing with Trouton's Rule, as modified by Walden, to apply to melting points. It is evident, then, that if the dextro isomer is associated to the same extent with itself as it is with the laevo isomer in the racemic compound, we should then get the same value of the ratio 1/T for the pure dextro isomer and for the 50% mixture with the laevo isomer, which is the criterion that Tammann uses to establish the absence of a racemic compound.

The value of K = 100k, where k is the "molecular depression" is abnormally high both in the case of camphor and of borneol. Indeed in the case of camphor the fact has been made use of by Rast [Ber. 1922, 1051], to devise a method of micro molecular weight determination by using camphor as a solvent.

If /

If we take

$$\frac{M \times \ell}{T} = 13.5$$

where M is the average molecular weight and ℓ the latent heat of fusion per gram. and T the absolute Temperature of melting,

then since. $K = \frac{RT^2}{\ell}$

$$\therefore \frac{\ell}{T} = \frac{RT}{K} = \frac{13.5}{M}$$

whence $M = \frac{13.5 \times K}{RT}$

Now for Camphor. $K = 40,000$

and $T = 451$

$$\therefore M = \frac{13.5 \times 40,000}{1.99 \times 451} = 602.$$

For Borneol. $K = 43,000$

and $T = 480$

$$\therefore M = \frac{13.5 \times 43,000}{1.99 \times 480} = 608.$$

In those cases we see that the value for the calculated molecular weight of camphor and borneol is very high, and would correspond to the existence of quadruple molecules. The evidence given by boiling point molecular weight determinations of these substances does not support this conclusion. The molecular weight of camphor in benzene ranges from 144-154 (Theoretical 152), and that of borneol in benzene ranges from 150-232 (Theoretical 154). Only in the case of borneol is there any evidence of association. The obvious conclusion is that camphor and borneol are among those substances for which the Rule $\frac{M \times \ell}{T} = 13.5$ does not apply.

Before proceeding to a mathematical analysis of the curve of types (1) and (3), it might be well to consider generally the equations which apply to substances at their melting points.

The ordinary law for the lowering of the melting point of a pure substance A by the addition of another pure substance B may be written as

$$\frac{dT}{dx_a} = \frac{RT^2}{L_a} \quad \text{---------- (1)}$$

Where /

Where T is the melting point on the absolute scale,

R is the gas constant

L_a is the latent heat of the substance A per gram molecule

x_a is the molar fraction of the substance A

if we write x_b as the molar fraction of the substance B then $x_a + x_b = 1$. The formula (1) only applies for small values of x_b, i.e. for values of x_a that approach unity.

Washburn and Read [Nat. Acad. Sc. 1915, 191] suggest that for the exact analysis of the melting point curves of two substances A and B we should use instead of the formula (1) of Van't Hoff, the expression

$$\frac{dT}{dx_a} = \frac{RT^2}{L_a x_a} \qquad (2)$$

and a corresponding expression for the substance B

$$\frac{dT}{dx_b} = \frac{RT^2}{L_b x_b} \qquad (2)'$$

On integrating the equation (1) we get

$$1 - x_a = \frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_{oA}}\right) \qquad (3)$$

and /

and on integrating the equation (2) we get

$$\log_e x_a = \frac{L}{R}\left(\frac{1}{T_{0A}} - \frac{1}{T}\right) \quad \text{------} \quad (4)$$

where T_{0A} represents the melting point of the pure substance A. For small values of x_b the equation reduces to

$$\log_e(1 - x_b) = \frac{L}{R}\left(\frac{1}{T_{0A}} - \frac{1}{T}\right)$$

$$\text{i.e.} \qquad x_b = \frac{L}{R}\left(\frac{1}{T} - \frac{1}{T_{0A}}\right)$$

which is the same as equation (3).

Instead of determining the latent heat of the substance A directly, it is possible by measuring the "molecular depression", i.e. the fall in temperature produced by adding one gram molecule of another substance to one hundred grams of A, to deduce the value for the latent heat of fusion L per gram molecule.

We have if k is the molecular depression then $K = 100k = RT^2/\ell$, where ℓ is the latent heat per gram. If M is the gram molecular weight then

$K = MRT^2/L$, and so $K/M = RT^2/L = dT/dx$ for values of x which approach unity.

For /

For such values of x_a the three expressions

$$\frac{dT}{dx} = \frac{RT^2}{L} \cdots (1); \quad \frac{dT}{dx} = \frac{RT^2}{Lx} \cdots (2); \quad \frac{dT}{dx} = \frac{K}{M} = \text{const} \cdots (5).$$

give the same form of curve.

DEXTRO and LAEVO PINENES.

If we consider the results for mixtures of dextro and laevo pinene first, since the curve in that case has a simple form, we can calculate values for the temperature of melting for the addition of various quantities of, say, laevo pinene, to pure dextro pinene, and this can be done using any one of the three equations (1), (2), or (5). The results and corresponding curves using equations (2) and (5) are found on pages 78-80. The results and corresponding curves using equation (1) are found on pages 81-83. For purposes of comparison the values of dt for each regular interval is shown. From an examination of the results it is evident that the values given by the straight line curve of equation (5) are in this particular case almost identical /

identical with the values given by the Washburn and Read equation (2). This, of course, is not usually the case. All the curves intersect at practically the 50% mixture, but the value for the melting temperature of the eutectic mixture is slightly lower than the value found by experiment in the case of the straight line curve. The value given by the Van't Hoff equation for the eutectic temperature is considerably higher than the experimental value, which is not surprising since the equation does not apply for such large amount of added substance. The experimental curve varies somewhat at other percentages from the straight line curve, but there is no doubt that in the case of d- and l- pinenes, we are dealing with a simple mixture of two substances, and the curve approximates closely to that given by an "ideal" solution.

The value of K for d- and l- pinene was found by determining the depression of the melting point produced by adding various quantities of toluene to pure d- and l- pinene, to be equal to 16500. Whence /

Whence L_a = the latent heat per gram molecule

= 717.0 for d- pinene

and L_b = 723.6 for l- pinene

also T_{oA}= 209 for d- pinene

and T_{oB}= 210 for l- pinene

If we apply Trouton's Rule to the pinenes, we get

$$M = \frac{13.5 \times 16500}{1.99 \times 210} = 533$$

this would give, as in the case of camphor and borneol, quadruple molecules. The molecular weight in benzene was determined by the freezing point method, and gave M = 137, which is practically the normal value (136). Here again it is obvious that the results given by Trouton's Rule are not in agreement with the results to be expected, or to those given by ordinary molecular weight determinations. The Hydrocarbons as a class do not exhibit any tendency to form associated molecules.

DEXTRO PINENE.

Melting Points

% d-pinene.	T	$t^{\circ}C$.	dt.
100	208.9	- 64.1	
90	196.9	- 76.1	12.0
80	185.0	- 88.0	11.9
70	173.2	- 99.8	11.8
60	162.1	-111.8	12.0
50	149.0	-124.0	12.2
40	136.3	-136.7	12.7

LAEVO PINENE.

% l-pinene.	T.	$t^{\circ}C$.	dt.
100	209.9	- 63.1	
90	197.7	- 75.3	12.2
80	186.0	- 87.0	11.7
70	174.1	- 98.9	11.9
60	162.1	-110.9	12.0
50	149.9	-123.1	12.2
40	137.3	-135.7	12.6

The above values for T were calculated using the formula $\frac{dT}{dx} = \frac{RT^2}{L_a x}$.

DEXTRO and LAEVO PINENES.

No. I is the experimental curve.

No. II, the straight line curve is given by the equation

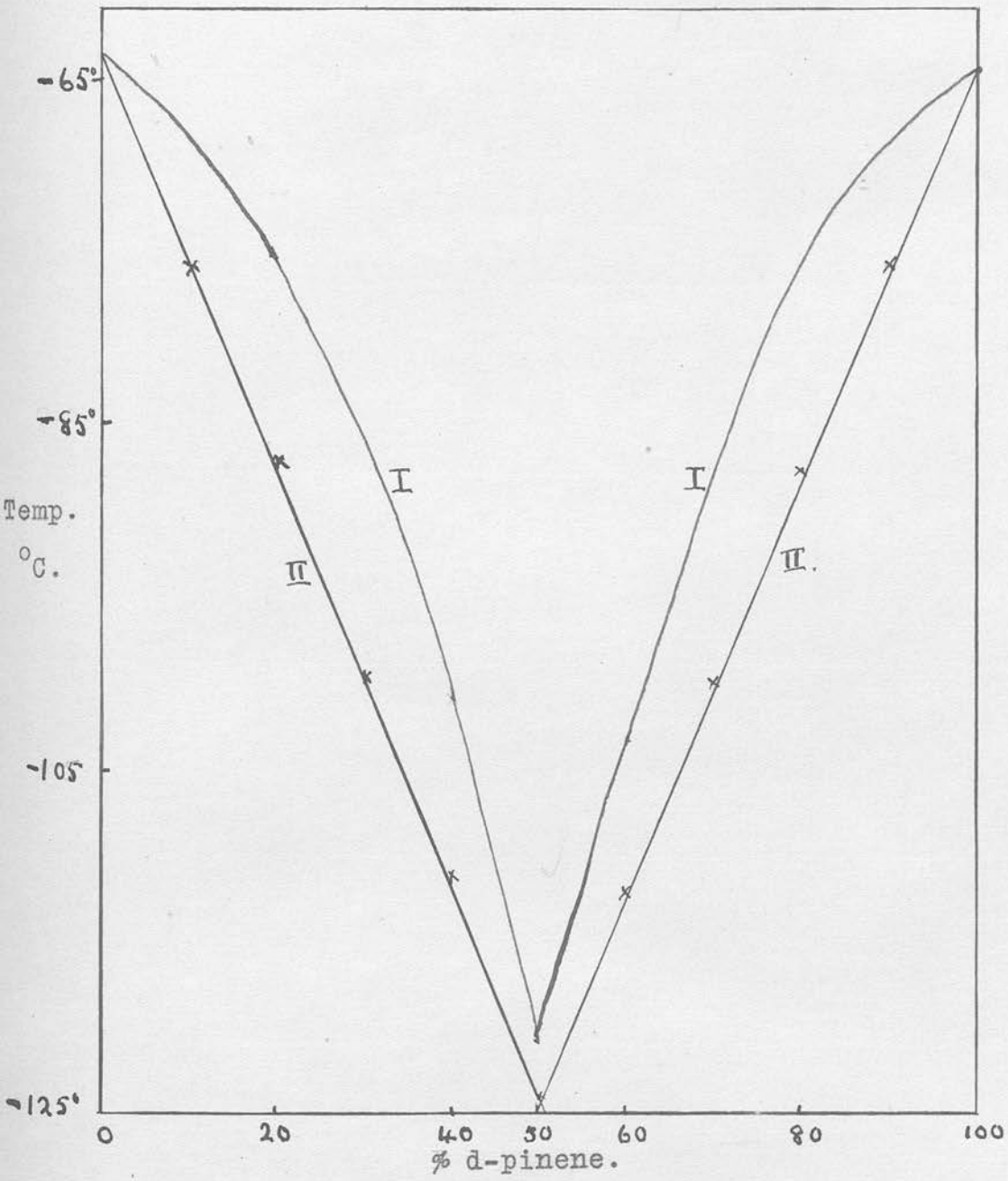
$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

The crosses indicate the points given by the equation

$$\frac{dT}{dx} = \frac{RT^2}{L_a x}$$

DEXTRO and LAEVO PINENES.

MELTING POINT CURVES.



DEXTRO PINENE.

Melting Points.

% d-pinene.	T.	t°C.	dt.
100	208.9	- 64.1	
90	197.5	- 75.5	11.4
80	187.2	- 85.8	10.3
70	177.9	- 95.1	9.3
60	169.6	-103.4	8.3
50	162.0	-111.0	7.6
40	155.0	-118.0	7.0

LAEVO PINENE.

% l-pinene.	T.	t°C.	dt.
100	209.9	- 63.1	
90	198.5	- 74.5	11.4
80	188.1	- 84.9	10.4
70	178.9	- 94.1	9.2
60	170.6	-102.4	8.3
50	162.9	-110.1	7.7
40	155.9	-117.1	7.0

The above values for T were calculated using the formula $\frac{dT}{dx} = \frac{RT^2}{L_a}$.

DEXTRO and LAEVO PINENES.

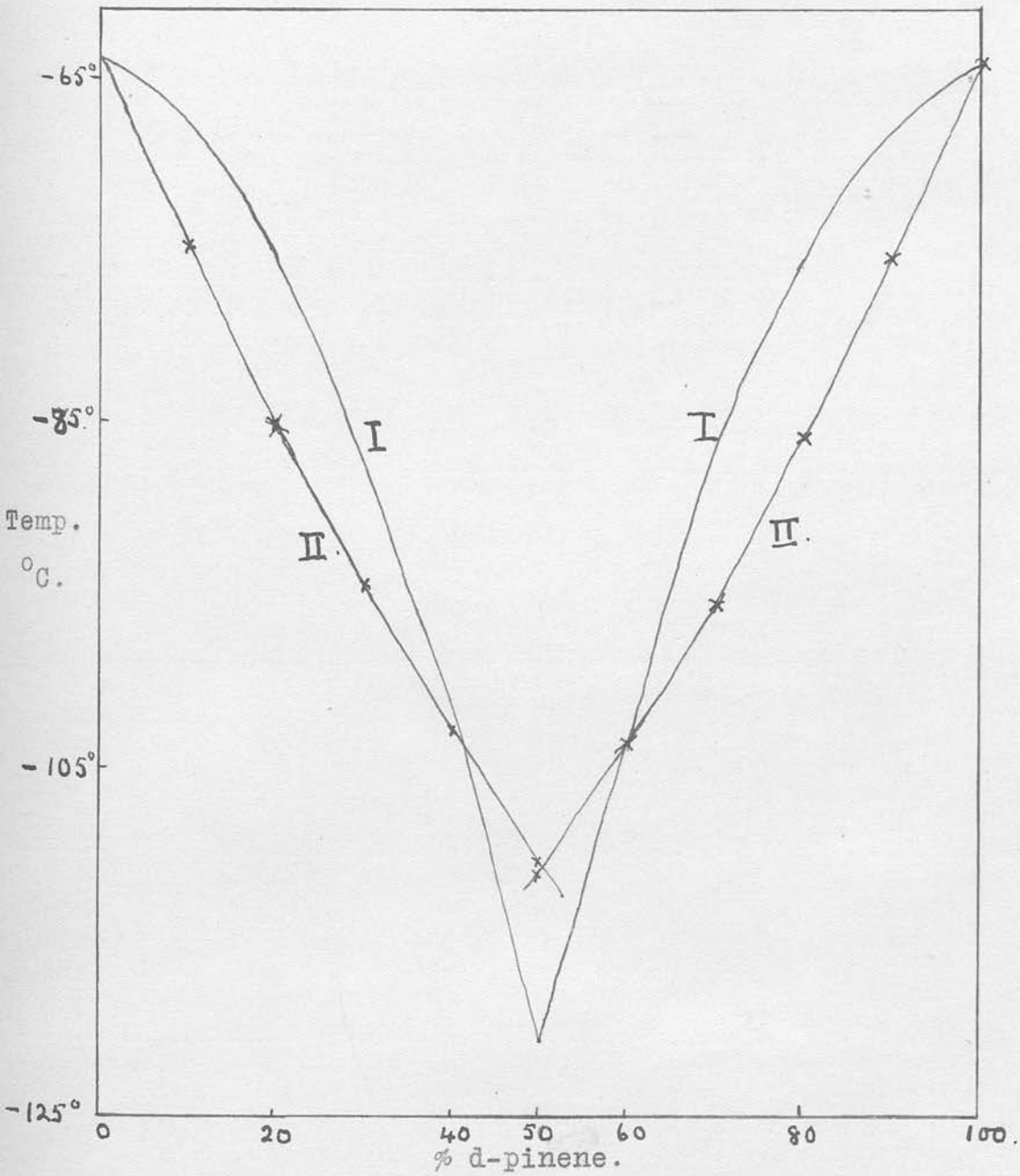
No. I is the experimental curve.

No. II is the curve given by the equation

$$\frac{dT}{dx} = \frac{RT^2}{La}.$$

DEXTRO and LAEVO PINENES.

MELTING POINT CURVES.



The other curves which are amenable to mathematical analysis are those obtained for camphoric acids and ortho methyl camphoric esters. In those cases the curves have to be considered in two sections;

(1) dextro acid in presence of racemic acid, and

(2) laevo acid in presence of racemic acid, and similarly for the esters.

DEXTRO and RACEMIC CAMPHORIC ACIDS.

In order to apply the equations (2) and (5) directly to a calculation of the gradients of an experimental curve, we must first plot the molecular percentage of the d- and r- acids against the corresponding values of t, the melting point temperature. The curve I is shown on page 94. By adding small quantities of acetanilide to the dextro acid, and finding the corresponding melting points, the average value of K = 100k where k is the "molecular depression", was calculated and found to be equal to 17500, the corresponding value of L, the molar latent heat of fusion, was 4835. The values of T given by the equation

$$\log_e x_a = \frac{L_a}{R}\left(\frac{1}{T_{oA}} - \frac{1}{T}\right)$$

where /

where L = 4835, R = 1.99, T_{oA} = 461, for x = 0.9, 0.8, 0.7, 0.6, 0.5, and 0.4 were calculated, and the results are shown in the table on page 92. The corresponding curve VI appears on page 94.

A similar calculation was made for the racemic acid, for which K = 13000, L = 13840, and T = 475.6. The table of results is shown on page 92. and the corresponding curve V on page 94.

The course of the curve calculated from the equation $\frac{dT}{dx} = \frac{RT^2}{L x}$ does not at all follow the course of the curve found by experiment.

The shape of the curve near the melting point of the racemic acid indicates the degree to which the acid is dissociated into its components. Kremann [Monat. 25,1215] has shown how the position of the curve may be found, if we assume definite percentages of dissociation of the compound. [Cf. Findlay and Hickmans J.C.S. 1907, 905].

(a) Assuming 20% dissociation of the racemic acid, the calculation was as follows:-

To calculate the dissociation constant k we have

20 x 20 = k(100-20), and so k = 5.

If /

If a is the amount of d- acid present due to dissociation, then if we add an amount of d- acid equal to x = 20%,

then (a + 20) a = k (100-a)

i.e. a (a + 20) = 5 (100-a)

i.e. a = 13.1

The amount of d- acid present = 33.1

The amount of l- acid present = 13.1

The amount of r- acid present = 86.9

If δ be the depression, then

$$\delta = \frac{46.1 \times 100}{133.1} \Delta = 34.61 \Delta$$

where $\Delta = \frac{K.}{100M} = \frac{13000}{100 \times 400} = .325°$

whence $\delta = 34.61 \times .325$, $\delta' = .43°C.$

A similar calculation for x = 40% gave

$\delta = 39.14 \times .325$, $\delta' = 1.89°C.$

The curve II was then drawn, representing 20% dissociation of the racemic acid, according to the following values for x and t. See page 94.

x	t°C.
0.0	202.6
0.2	202.2
0.4	200.7

(b) /

(b) Assuming 15% dissociation, we get

for x = 20% $\delta = 28.40\Delta$, $\delta' = 0.75^{\circ}C.$

for x = 40% $\delta = 35.05\Delta$, $\delta' = 2.91^{\circ}C.$

The curve III was then drawn, representing 15% dissociation of the racemic acid, according to the following values for x and t. Curve on page 94.

x	t°C.
0.0	202.6
0.2	201.9
0.4	199.7

(c) Assuming 10% dissociation, we get

for x = 20% $\delta = 23.10\Delta$, $\delta' = 1.60^{\circ}C.$

for x = 40% $\delta = 31.62\Delta$, $\delta' = 4.37^{\circ}C.$

The curve IV was then drawn, representing 10% dissociation of the racemic acid, according to the following values for x and t. Curve on page 94.

x	t°C.
0.0	202.6
0.2	201.0
0.4	198.3

The experimental curve lies between the curve for 15% dissociation and the curve for 10% dissociation /

dissociation. The degree of dissociation of the racemic acid was thus taken as equal to 12%. Assuming this value of 12% dissociation, we can calculate what the melting point of the pure racemic acid would be if there were no dissociation.

$$\delta = \frac{24 \times 100}{112} \Delta = 21.43 \Delta$$

$$= 21.43 \times .325 = 6.96$$

therefore $t = 202.6 + 6.96 = 209.6^{\circ}C.$

Taking this value as the melting point of the pure racemic acid, we have drawn the straight line curve II, page 97 with $dT/dx = K/M = 32.5$ and the straight line curve III, page 97 with $dT/dx = K/M = 17500/200 = 87.5$ was drawn for the dextro acid.

These two straight lines give the percentage of eutectic mixture fairly accurately, but the eutectic temperature found is higher.

The curves were drawn again on the assumption that we were dealing with r- acid and 2d- acid. The table of calculated results is shown on page 98 and the corresponding curve on page 100. The melting point of the pure racemic acid would now be $206.5^{\circ}C.$ if /

if we assume it to be dissociated, as already mentioned, into 2d- and 2l- acids to the extent of 12%.

Thirdly, the curve was drawn on the assumption that the d- acid was associated with the d- acid to the same extent as it is associated with the l- acid in the racemic compound, so that the average value for the size of the dextro molecule may be taken as equal to 1.8d. The melting point of the pure racemic acid would now be 206.8°C. if we assume it to be dissociated into 1.8d acid and 1.8l acid to the extent of 12%. The table of calculated results is on page 101, and the corresponding curve on page 103.

All the three curves give about equally well the eutectic percentage, but not accurately the eutectic temperature. It is obvious that no assumption with regard to the molecular complexity of the d- and l- acid will give two straight lines intersecting both at the eutectic temperature and at the eutectic percentage. The reason for this may be that in calculating the gradient, we have taken into account only the latent heat of fusion, and not the possible /

possible heat of dilution of d- and r- acid, or the heat of dissociation of those acids.

Van Laar [cf. Kremann Monat. 28] has worked out a formula for α the degree of dissociation of a compound in terms of known values. Kremann found that the values given by this formula were about twice as large as those given by his graphical method. It was thought to be interesting to see what the formula would give for the substance under consideration. The calculation is as follows:-

Van Laar's formula is

$$\alpha = \frac{RT^2}{L} \cdot \frac{x^2(1+x)}{4(T_0 - T)}$$

which gives for racemic acid since

$$\frac{RT^2}{L} = \frac{K}{M}, \quad \alpha = \frac{K}{M} \cdot \frac{x^2(1+x)}{4(T_0 - T)}$$

$$\therefore \alpha = \frac{13000}{400} \cdot \frac{\cdot 04 \times 1 \cdot 2}{4 \times 1 \cdot 2} = \cdot 32.$$

The value for the degree of dissociation given by this calculation is nearly 2 ½ times as great as that given by the graphical method. This value would, of course, be reduced if we took into account the possible heat of dilution and the heat of dissociation.

Evidence /

Evidence for the molecular complexity of Camphoric acid is somewhat difficult to obtain. The acid unfortunately is not sufficiently soluble in benzene, to render a molecular weight determination in that solvent available. In alcohol the molecular weight is rather less than the normal, but that is not a surprising result, since alcohol generally gives low results even with associated substances. The general behaviour of organic acids would show that they, as a class, are associated.

Applying as before Trouton's Rule, we get for dextro acid

$$M = \frac{13{\cdot}5 \times 17500}{1{\cdot}99 \times 461} = 258. \text{ (Theor. 200)}.$$

for racemic acid

$$M = \frac{13{\cdot}5 \times 13000}{1{\cdot}99 \times 475{\cdot}6} = 185. \text{ (Theor. 400)}.$$

The conclusion to be drawn from this is that the d-acid is associated to the extent of about 30%, but there is no evidence of association of the r-acid. Trouton's Rule then gives a general indication that here we are dealing with associated molecules, but that the racemic acid is largely dissociated.

DEXTRO CAMPHORIC ACID.

Melting Points.

% d-acid.	T.	$t^{o}C$.	dt.
100	461.2	188.2	
90	451.8	178.8	9.4
80	442.2	169.2	9.6
70	431.7	158.7	10.5
60	420.3	147.3	11.4
50	407.3	134.3	13.0
40	392.5	119.5	14.8

RACEMIC CAMPHORIC ACID.

% r-acid.	T.	$t^{o}C$.	dt.
100	475.6	202.6	
90	472.4	199.4	3.2
80	468.7	195.7	3.7
70	464.5	191.5	4.2
60	460.0	187.0	4.5
50	454.0	181.0	6.0
40	447.5	174.5	6.5

The above values for T were calculated using the formula $\frac{dT}{dx} = \frac{RT^2}{L_a x}$.

DEXTRO and RACEMIC CAMPHORIC ACIDS.

No. 1 is the experimental curve plotted for molecular % d-acid and r-acid.

No. 11 is the curve for 20% dissociation of the racemic acid.

No. 111 is the curve for 15% dissociation of the racemic acid.

No. 1V is the curve for 10% dissociation of the racemic acid.

No. V is the curve given by the equation

$$\frac{dT}{dx} = \frac{RT^2}{L_a x}$$

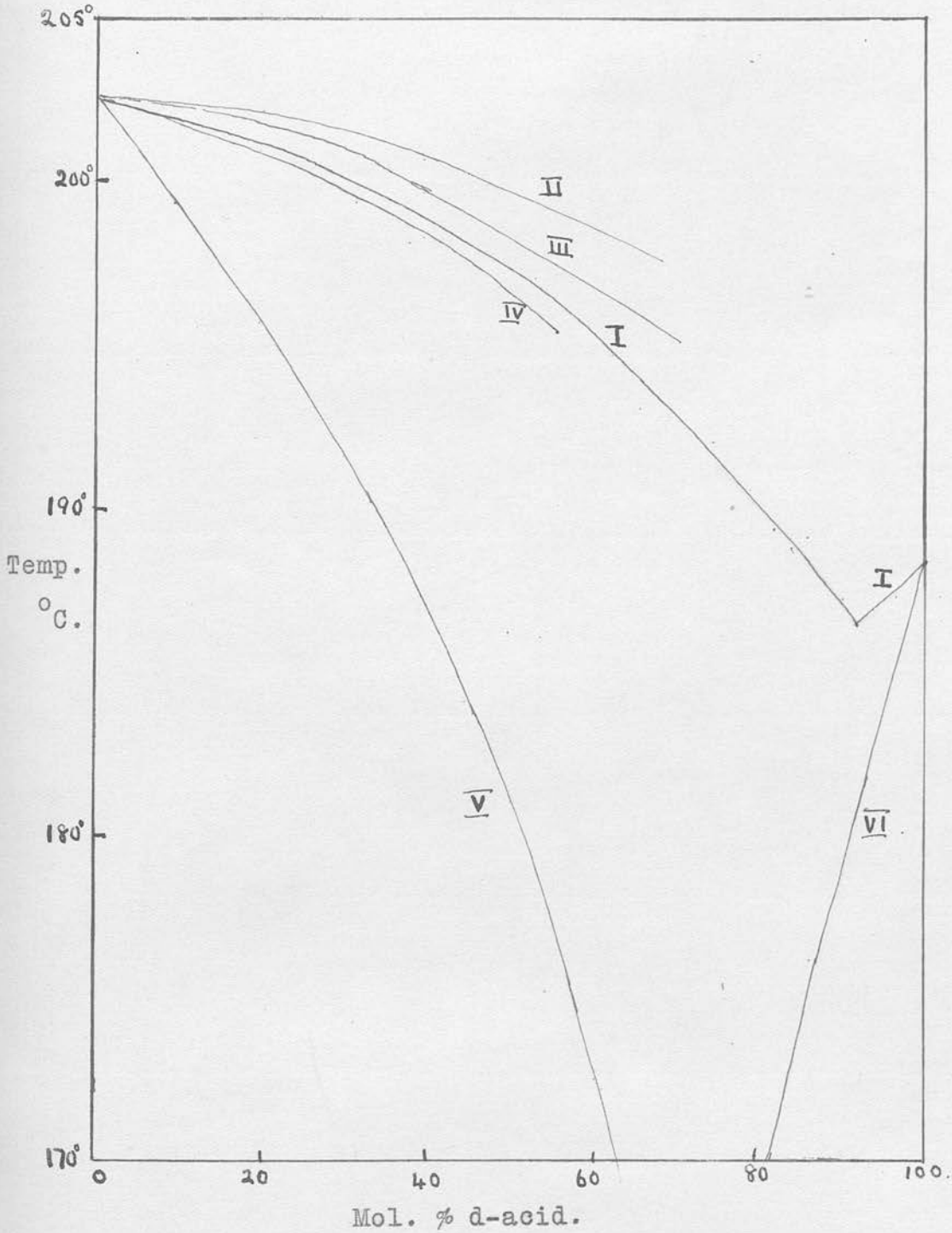
for racemic acid.

No. V1 is the curve given by the equation

$$\frac{dT}{dx} = \frac{RT^2}{L_a x}$$

for dextro acid.

DEXTRO and RACEMIC CAMPHORIC ACIDS.



DEXTRO and RACEMIC CAMPHORIC ACIDS.

Mol. % d-acid.	Melting Point in °C.
100.00	188.2
96.62	187.3
92.12	186.4
90.42	187.2
86.07	189.1
81.90	189.3
65.91	193.1
62.84	194.7
53.37	197.1
38.23	198.1
27.60	200.5
0.00	202.6

DEXTRO and RACEMIC CAMPHORIC ACIDS.

No. 1 is the experimental curve plotted for molecular % d-acid and r-acid.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for racemic acid, assuming 12% dissociation of the racemic acid.

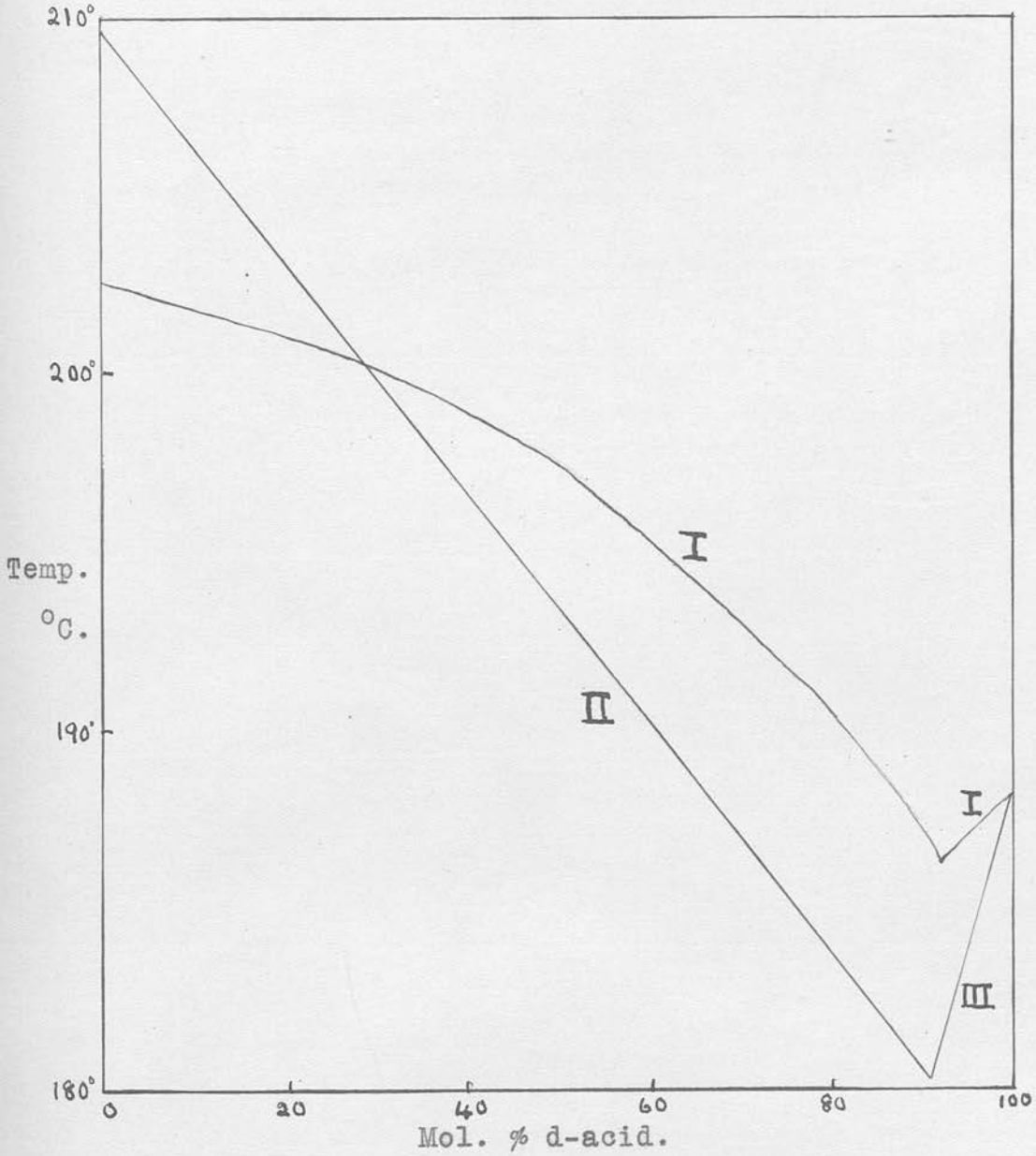
No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for dextro acid.

DEXTRO and RACEMIC CAMPHORIC ACIDS.

MELTING POINT CURVES.



DEXTRO and RACEMIC CAMPHORIC ACIDS.

Mol. % 2d-acid.	Melting Point in °C.
100.00	188.2
93.48	187.3
85.40	186.4
81.72	187.2
75.57	189.1
69.38	189.3
49.17	193.1
45.77	194.7
36.39	197.1
23.63	198.1
16.01	200.5
0.00	202.6

DEXTRO and RACEMIC CAMPHORIC ACIDS.

No. 1 is the experimental curve plotted for molecular % 2 d-acid and r-acid.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for racemic acid, assuming 12% dissociation of the racemic acid.

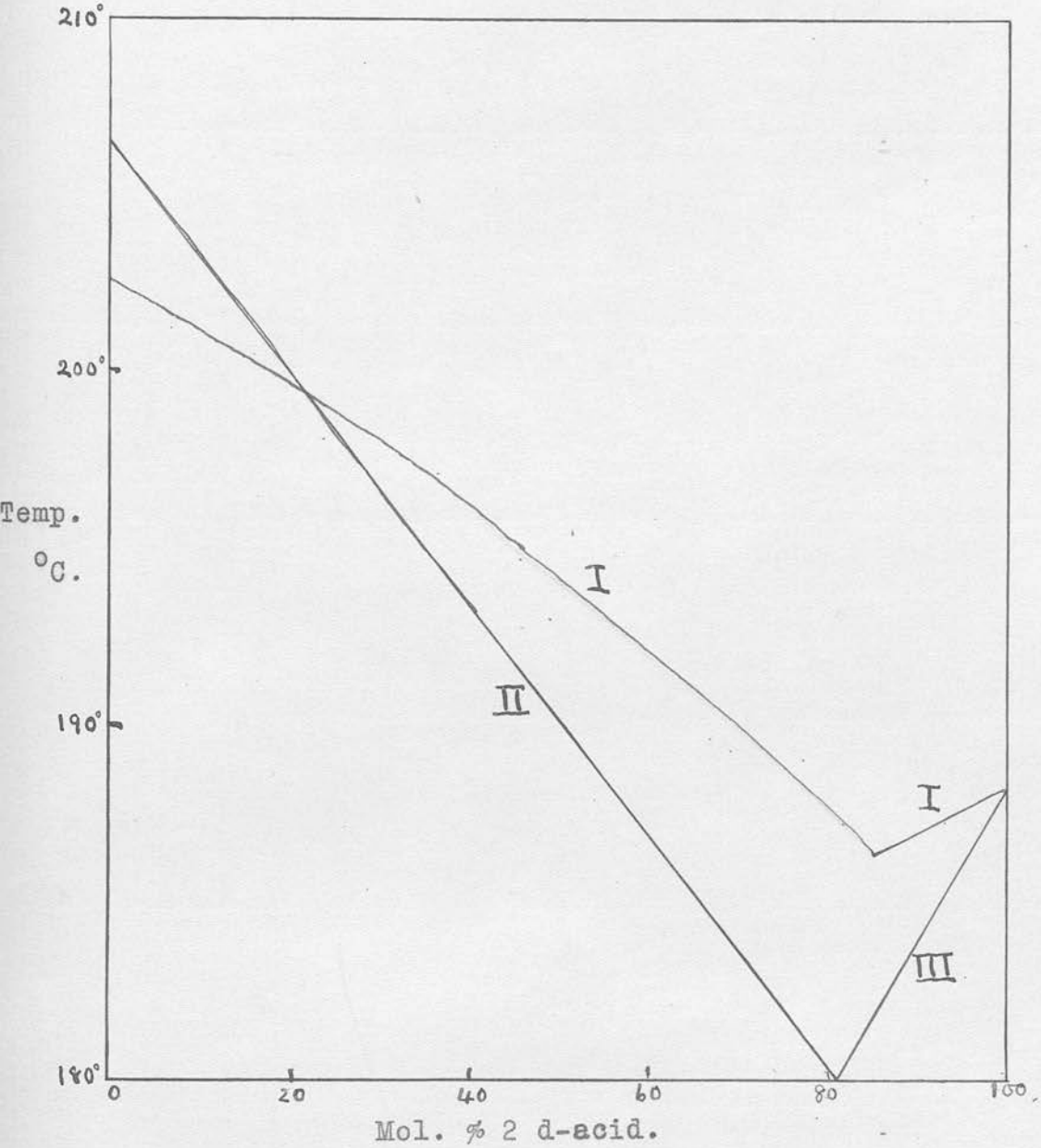
No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for 2 d-acid.

DEXTRO and RACEMIC CAMPHORIC ACIDS.

MELTING POINT CURVES.



DEXTRO and RACEMIC CAMPHORIC ACIDS.

Mol. % 1.8 d-acid.	Melting Point in °C.
100.00	188.2
94.10	187.3
86.68	186.4
84.01	187.2
77.47	189.1
71.56	189.3
51.81	193.1
48.40	194.7
38.87	197.1
25.58	198.1
17.48	200.5
0.00	202.6

DEXTRO and RACEMIC CAMPHORIC ACIDS.

No. 1 is the experimental curve plotted for molecular % 1.8 d-acid and r-acid.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for racemic acid, assuming 12% dissociation of the racemic acid.

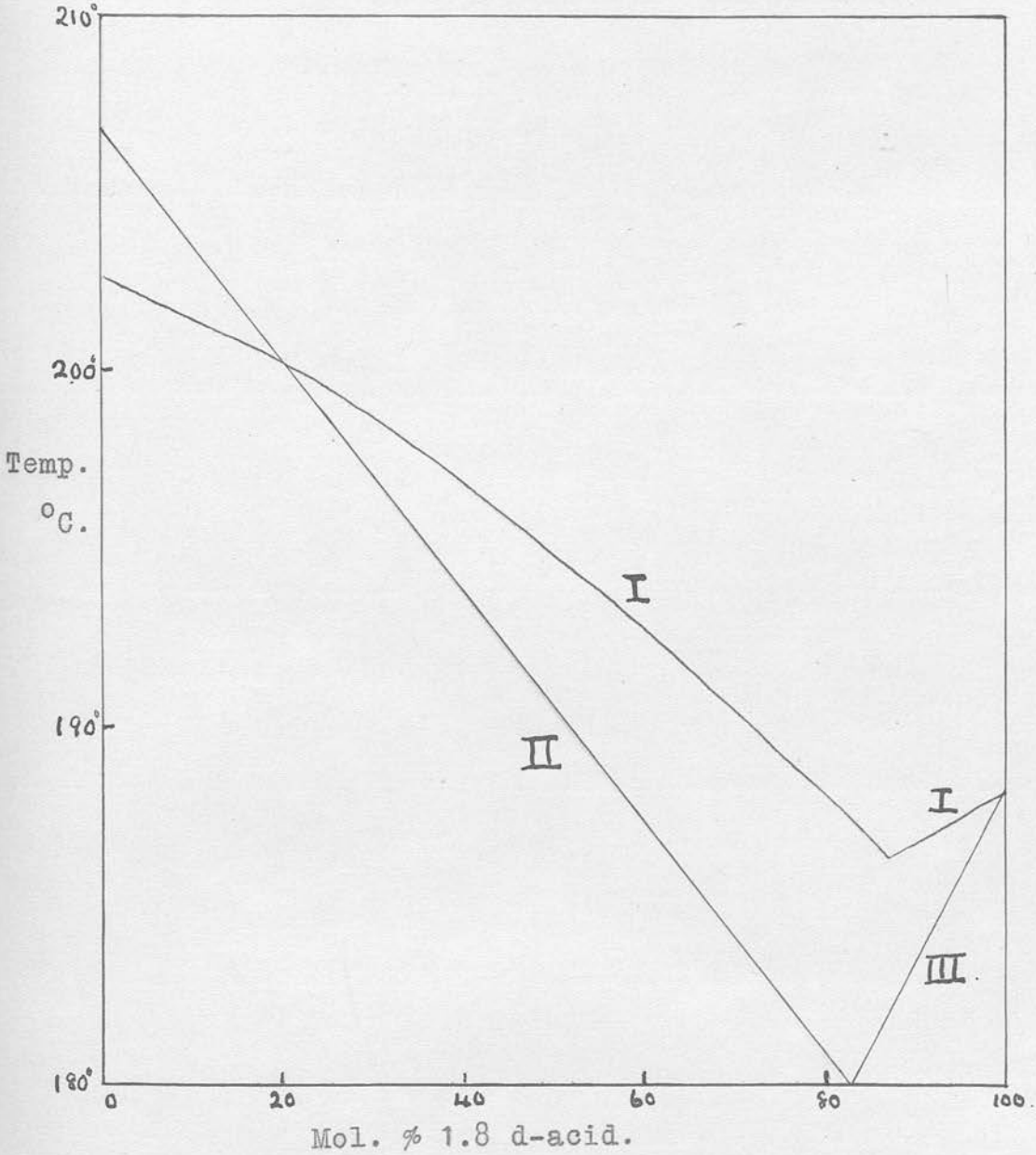
No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for 1.8 d-acid.

DEXTRO and RACEMIC CAMPHORIC ACIDS.

MELTING POINT CURVES.



DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

As in the case of camphoric acids we have first to plot the molecular percentage of the dextro and racemic esters against the corresponding values of t, the melting point temperature. This has been done in table on page 113 and the curve is shown on page 115. By adding small quantities of Urethane to the dextro ester, and finding the corresponding melting points, the average value of K was found to be equal to 23000, and the corresponding value of L was found to be equal to 2234. The values of T given by the equation $\hat{T} = \frac{K}{L + x}$ (2) were then calculated for the following values of x.

x = 0.9, 0.8, 0.7, 0.6, 0.5, and 0.4.

The table of results is shown on page 110 and the corresponding curve V on page 112.

A similar calculation was made for the racemic ester, for which K = 18800, L = 5838, and T = 359. The table of results is shown on page 110, and the corresponding curve IV on page 112.

By a similar calculation to that employed in the case of camphoric acid, we can draw curves for /

for various percentages of dissociation of the racemic compound.

(a) Assuming 20% dissociation, we get

for x = 20% $\delta = 34.61\Delta$, $\delta' = 0.5^{\circ}C.$

for x = 40% $\delta = 39.14\Delta$, $\delta' = 2.5^{\circ}C.$

The curve III was then drawn, representing 20% dissociation of the racemic ester, according to the following values for x and t. Curve on page 112.

x	$t^{\circ}C.$
0.0	85.9
0.2	85.4
0.4	83.4

(b) Assuming 15% dissociation, we get

for x = 20% $\delta = 28.40\Delta$, $\delta' = 1.0^{\circ}C.$

for x = 40% $\delta = 35.05\Delta$, $\delta' = 3.9^{\circ}C.$

The curve II was then drawn, representing 15% dissociation of the racemic ester, according to the following values for x and t. Curve on page 112.

x	$t^{\circ}C.$
0.0	85.9
0.2	84.9
0.4	82.0

The /

The experimental curve lies between the curve for 20% dissociation and the curve for 15% dissociation. The degree of dissociation of the racemic ester was thus taken as equal to 18%. Assuming this value of 18%, the melting point of the pure racemic ester, if there had been no dissociation, would have been 99.4°C.. Taking this value as the melting point of the pure racemic ester, we have drawn the straight line curve II, page 115 with

$dT/dx = K/M = 18800/428 = 43.9$

and the straight line curve III, page 115 with

$dT/dx = K/M = 23000/214 = 107.5.$

was drawn for the pure dextro ester.

These two straight line curves intersect at a point, where the percentage of dextro isomer at the eutectic percentage is slightly higher than the experimental value. The value of the eutectic temperature is lower than for the experimental curve. The curves were drawn again on the assumption that we were dealing with r- ester and 2d- ester. The table of calculated results is shown on page 116 and the corresponding curve on page 118. The melting point /

point of pure racemic ester would now be 94.8°C., on the above assumption.

Thirdly, the curve was drawn on the assumption that the d-ester was associated with the d-ester to the same extent as it is associated with the l- ester in the racemic compound, so that the average value for the size of the dextro molecule may be taken as equal to 1.7d.. The melting point of the pure racemic ester would now be 95.0°C. if we assume it to be dissociated into 1.7d ester and 1.7l ester to the extent of 18%. The table of calculated results is on page 119 and the corresponding curve on page 121.

In the case of the ester, the curves for 2d and 1.7d ester give very good agreement for the eutectic percentage, and the eutectic temperature is not so much below the experimental value as in the case of the acid. It is probable, therefore, that the heat of dilution and the heat of dissociation are not such important factors in the case of the ester, as they are in the case of the acid.

Calculating α the degree of dissociation of /

of the racemic ester in terms of Van Laar's formula, we get

$$\alpha = \frac{18800}{428} \times \frac{\cdot 04 \times 1 \cdot 2}{4 \times \cdot 75} = \cdot 70.$$

The value for the degree of dissociation given by this calculation is nearly three and a half times as great as that given by the graphical method.

Evidence for the molecular complexity of the ester was obtained as follows:-

The molecular weight of the ester was found by the boiling point method, using benzene as solvent, to be equal to 325, showing that there is a considerable amount of association of the ester.

Applying as before Trouton's Rule, we get for dextro ester

$$M = \frac{13 \cdot 5 \times 23000}{1 \cdot 99 \times 347 \cdot 4} = 449. \text{ (Theor. 214)}$$

for racemic ester

$$M = \frac{13 \cdot 5 \times 18800}{1 \cdot 99 \times 359} = 355. \text{ (Theor. 428)}$$

The conclusion to be drawn from this is that the d-ester gives double molecules, and that the racemic ester is dissociated to the extent of about 30%.

The /

The values of the melting points of the ester mixture are more reliable than those found in the case of the acid, because there was no sign of decomposition in the case of the melted ester. The only difficulty was that the ester tended to remain as an oil for a long time, so that calorimetric determinations for the heat data were not available.

DEXTRO METHYL CAMPHORIC ESTER.

Melting Points.

% d-ester.	T.	t°C.	dt.
100	347.4	74.4	
90	336.4	63.4	11.0
80	324.9	51.9	11.5
70	312.7	39.7	12.2
60	299.9	26.9	12.8
50	286.0	13.0	13.9
40	270.4	-2.6	15.6

RACEMIC METHYL CAMPHORIC ESTER.

% r-ester.	T.	t°C.	dt.
100	359.0	86.0	
90	354.5	81.5	4.5
80	349.6	76.6	4.9
70	344.0	71.0	5.6
60	337.9	64.9	6.1
50	331.0	58.0	6.9
40	322.8	49.8	8.2

The above values for T were calculated using the formula $\frac{dT}{dx} = \frac{RT^2}{L_a x}$.

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

No. I is the experimental curve.

No. II is the curve for 15% dissociation of racemic ester.

No. III is the curve for 20% dissociation of racemic ester.

No. IV is the curve given by the equation

$$\frac{dT}{d\kappa} = \frac{RT^2}{L_a \kappa}.$$

for racemic ester.

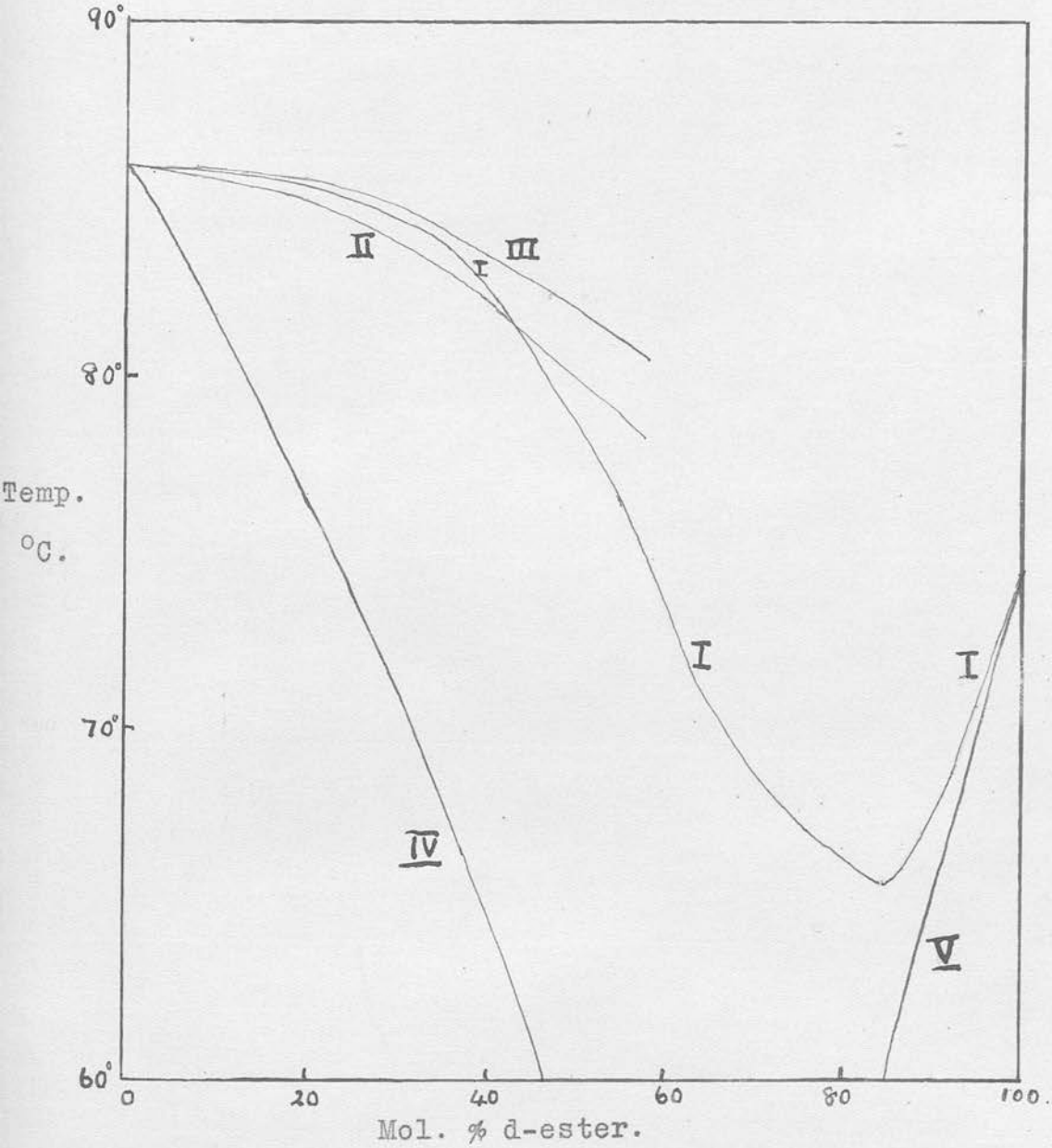
No. V is the curve given by the equation

$$\frac{dT}{d\kappa} = \frac{RT^2}{L_a \kappa}.$$

for dextro ester.

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

MELTING POINT CURVES.



DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

Mol. % d-ester.	Melting Point in °C.
100.00	74.4
94.88	70.5
91.96	68.7
88.92	67.0
86.25	65.9
84.44	65.6
79.63	66.6
75.08	67.6
68.08	68.0
63.50	70.2
58.45	74.8
41.29	82.2
38.55	83.3
17.85	85.5
2.82	85.7
0.00	85.9

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

No. 1 is the experimental curve plotted for molecular % d-ester and r-ester.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

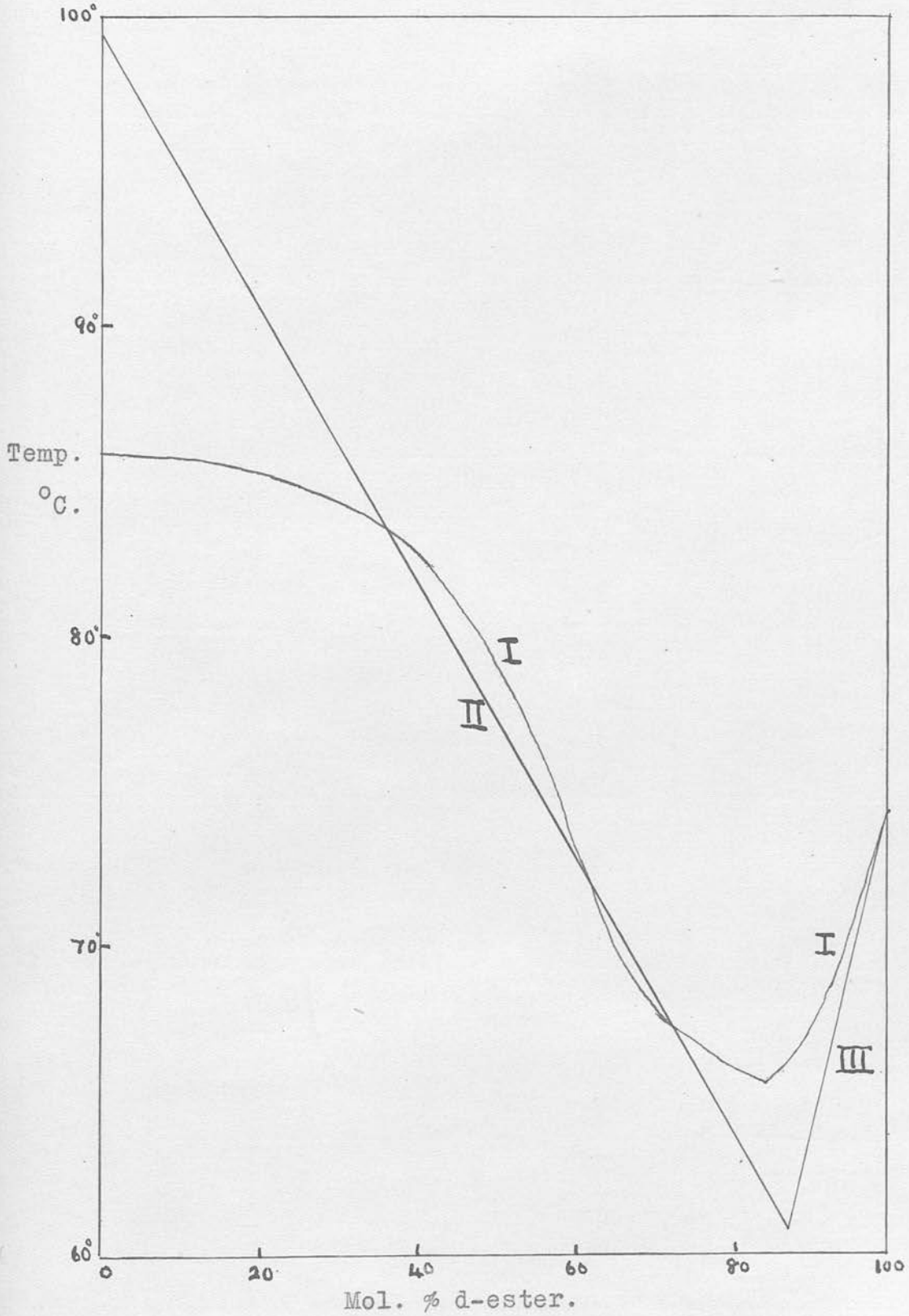
for racemic ester, assuming 18% dissociation of the racemic ester.

No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for dextro ester.

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.



DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

Mol. % 2d-ester.	Melting Point in °C.
100.00	74.4
90.28	70.5
85.10	68.7
80.04	67.0
75.81	65.9
73.08	65.6
66.18	66.6
60.24	67.6
51.61	68.0
46.51	70.2
41.29	74.8
26.01	82.2
22.56	83.3
9.90	85.5
1.43	85.7
0.00	85.9

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

No. 1 is the experimental curve plotted for molecular % 2 d-ester and r-ester.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

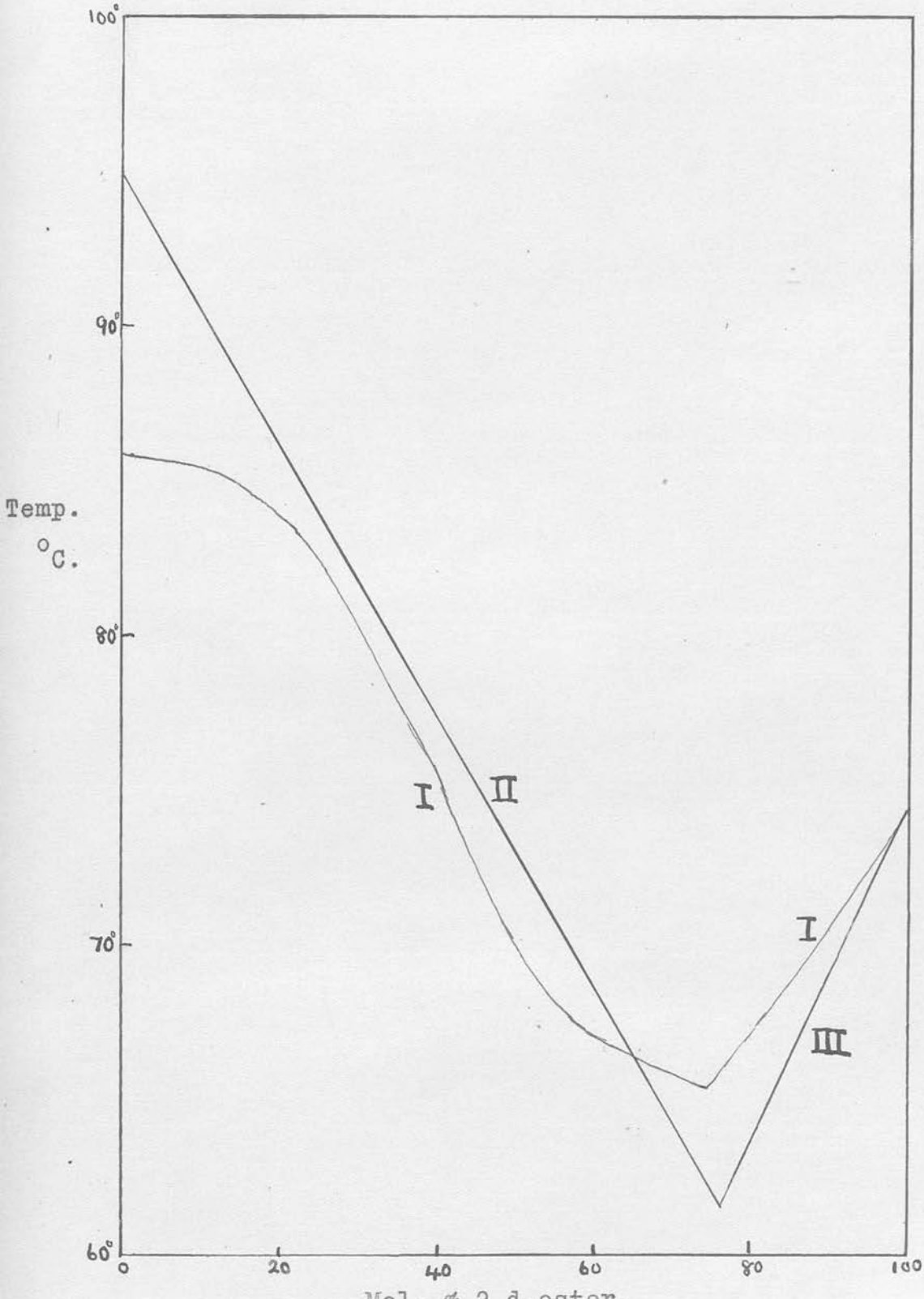
for racemic ester, assuming 18% dissociation of the racemic ester.

No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for 2 d-ester.

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.



DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

Mol. % l.7 d-ester.	Melting Point in °C.
100.00	74.4
91.62	70.5
87.04	68.7
82.50	67.0
78.67	65.9
76.15	65.6
69.71	66.6
64.06	67.6
55.64	68.0
50.57	70.2
45.28	74.8
29.26	82.2
25.53	83.3
11.44	85.5
1.67	85.7
0.00	85.9

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.

No. 1 is the experimental curve plotted for molecular % 1.7 d-ester and r-ester.

No. 11, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

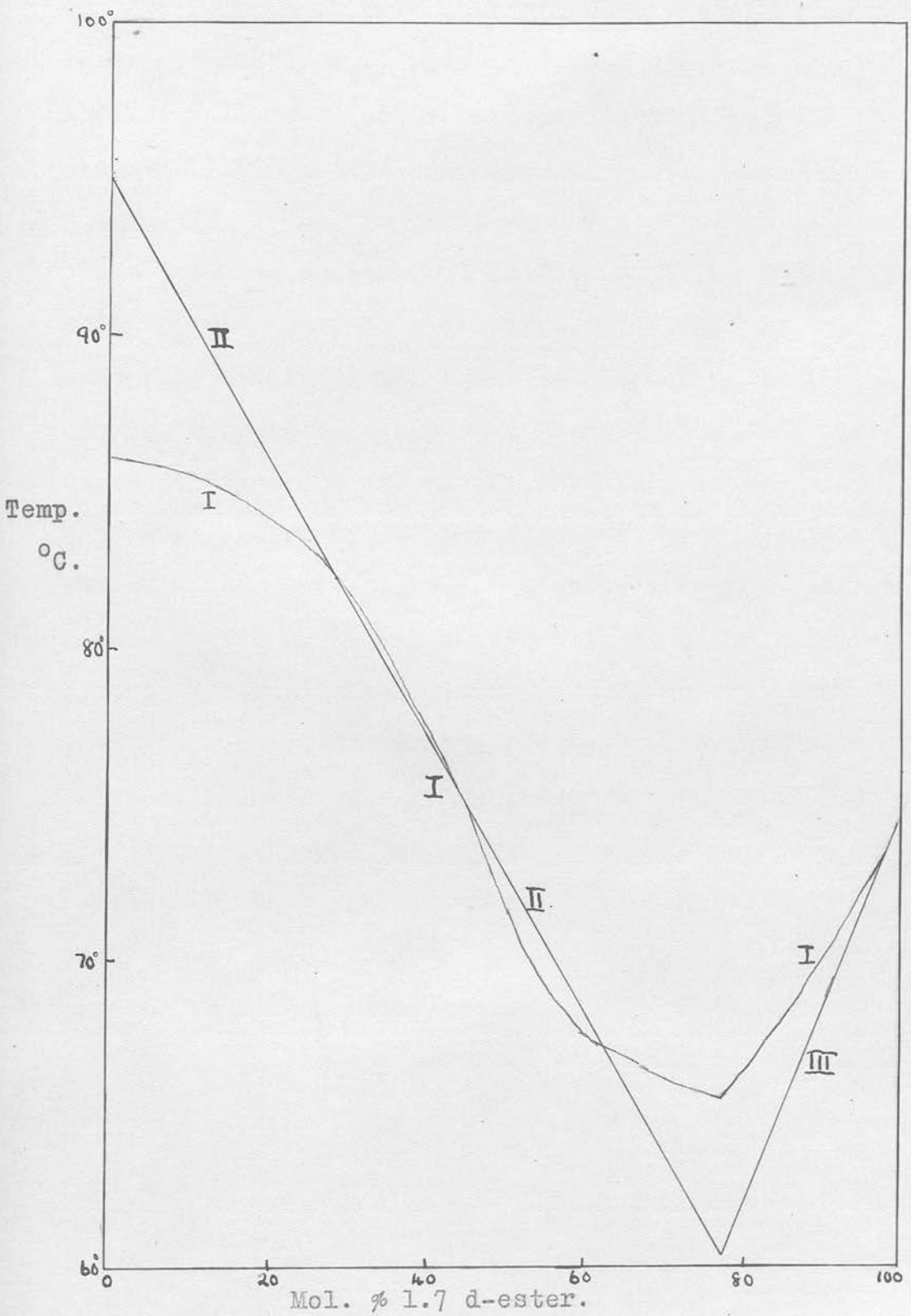
for racemic ester, assuming 18% dissociation of the racemic ester.

No. 111, the straight line curve, is given by the equation

$$\frac{dT}{dx} = \frac{K}{M} = \text{const.}$$

for 1.7 d-ester.

DEXTRO and RACEMIC METHYL CAMPHORIC ESTERS.



DISCUSSION of RESULTS.

If we arrange substances in the order of their associating power, we obtain a sequence somewhat as follows:- Hydrocarbons, Anhydrides, Ketones, Alcohols, Acid Esters, and Acids.

Group I. The two hydrocarbons studied, namely, pinene and camphene, showed different types for their melting point curves. The type for pinene is that of a (dl) conglomerate, a simple mixture of d- and l-pinene, with no evidence of a racemic compound. The curve for camphene is that of the mixed crystal type. Both substances, by determination of their molecular weight by the freezing point method, using benzene as solvent, give normal molecular weight. There is no direct evidence of association of the molecules of the pure substances in either case. They are closely related to one another, and indeed the only striking difference between them is the considerable one between the temperatures at which they melt. The difference, then, must be one depending on the temperature. We find generally that a rise of temperature favours the formation of mixed crystals (see Bruni's "Feste /

"Feste Losungen"), and so it is not surprising that when we are dealing with such similar substances as Optical Isomers, the dextro form should be able to replace the laevo form in the crystal without appreciably altering its shape or melting point. The fact that so many mixed crystal types of curve are found for Optical Isomers, and only one, namely the case of pinene now described, yields a simple (dl) conglomerate points to the conclusion that in many cases where we might expect to get a simple mixture curve, we obtain a mixed crystal curve. The fact that we get no racemic compound in the case of pinene has already been concluded by Mitchell and Smith [J.C.S. 1913, 489] from considerations of molecular surface energy, and by Pope and Peachey [J.C.S. 1899, 1111] from differences of rotation in various solvents.

Group II. The mixed crystal type of curve is by far the most common type, and in this investigation is given by a hydrocarbon (camphene), ketone (camphor), alcohol (borneol), anhydride, and acid ester (bornyl hydrogen phthalate).

It has already been shown that this type of curve does not preclude the existence of a racemic compound /

compound. It should be noted that in the case of the acid ester here included, namely, bornyl hydrogen phthalate, the part conferring optical activity is not in the acidic part of the molecule, which is the part that confers associating power. It is in this respect essentially different from that of the other acid ester studied, namely, ortho methyl camphoric ester, which falls into group III. In the case of Octyl Hydrogen Phthalate already studied by Dunstan and Thole [J.C.S. 1910, 1249], it was concluded from viscosity determinations that there was no racemic compound formed. The hydrocarbon, anhydride, and ketone, which fall into this group, show no evidence of association of the pure optical isomers, and as the temperatures of melting are all comparatively high we might expect the mixed crystal type of curve in place of the curve denoting a simple mixture. In the case of the alcohol studied (borneol), we have evidence of a slight amount of association, and so we might expect that the racemic compound, if formed, would be largely dissociated. In view of the fact that d- camphor and d- borneol form mixed crystals so readily, (see curve on page 40), we might expect to find /

find that d- borneol would form mixed crystals readily with l- borneol, and with r- borneol, especially if the latter is only present to a small extent. From these results we conclude that this type of curve is given by substances which show little or no associating power in the pure isomer.

Group III. This type exhibits the definite formation of a racemic compound. It includes the two substances which might be expected to do so, since they belong to groups of substances which generally show associated molecules. By calculation it is shown that in both cases the racemic compound formed is only dissociated to a small extent, in the case of the acid to the extent of 12%, and in the case of the ester to the extent of 18%. In both cases, then, we have shown that at the temperature of melting the racemic compound is present to a large extent in the liquid state. In both cases an examination of the curves will show that the theoretical curves agree well with the experimental curves, especially as regards the percentage of eutectic compound, and that the discrepancy with regard to the eutectic temperature may be accounted for by considering the heat of dilution /

dilution and the heat of dissociation, which had not been taken into account in drawing the curve, as no exact values for them could be obtained.

Broadly, then, the strongly associating substances show distinct evidence of formation of racemic compounds, and belong to curves of group III. Substances with feebly associating power furnish curves of group II, where the formation of a racemic compound is possible. Substances which show no associating power may be found in group I, where we have definite evidence of the absence of a racemic compound, or to group II, where its absence is very probable. Since the associating power of substances may vary continuously, and since the percentage dissociation of a racemic compound is also subject to continuous variation, we might expect to find the one type of curve merging into the other. The larger the percentage of dissociation of a racemic compound, the more closely will the type of curve in group III approximate to the type of curve in group II.

The results of this investigation are in agreement with those already obtained. Thus Centnerzwer [Zeit. Phys. Chem. 1899, 29, 715] in his study /

study of the melting point curves of a number of optically active acids and esters has shown that they all exhibit curves belonging to the type of group III, showing the existence of racemic compounds. Bromo-Camphor and Chloro-Camphor belong to type of group II [Pope, J.C.S. 1895, 388]. Vanzetti, using a calorimetric method, found inactive camphor to be a solid solution of the two components, [Atti, Accad. Lincei, 22 II, 479]. Adriani [Zeit. Phys. Chem. 1900, 33, 453] found that dimethyl tartaric ester, diacetyl tartaric ester, and phenyl glycollic acid, formed racemic compounds giving curves of type in group III.

A general review of the position with regard to racemates and pseudoracemates was given by Landrieu in 1922 [Bull. Soc. Chim. 31, 1234]. He advanced the view that if the dextro and laevo isomers could form ions as in the case of acids or salts, they would tend to form racemic compounds, i.e. give curves of type of group III. If on the other hand they are non-dissociable, they would only form mixed crystals, and give curves of type of group II. This conclusion is in agreement with the /

the results of the above experiments. Since polar compounds are those which give associated compounds, they are also those which give rise to racemic compounds. The fundamental reasons for the formation of racemic compounds are no better understood than those for the formation of associated substances, and it may be that electrical forces are the main factors in both. [See Turner's "Molecular Association"].

C O N C L U S I O N.

It has been shown that substances which do not associate, or do so only to a slight extent, yield melting point curves for their optical isomers which either definitely show the absence of a racemic compound, or show that it is unlikely to be present to any large extent.

Secondly, substances which are definitely known to associate show the existence of a racemic compound from the investigation of their melting point curves, and the theoretical curves, which have /

have been drawn, agree well with the assumption that the dextro isomer is associated with itself in the pure isomer to the same extent as it is associated with the laevo isomer in the racemic compound.